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CIV.—*A New Method for the Measurement of Hydrolysis in Aqueous Solution based on a Consideration of the Motion of Ions.*

By ROBERT BECKETT DENISON, M.Sc., Ph.D., and BERTRAM DILLON STEELE, D.Sc.

DURING the development of a more accurate method (Denison and Steele, *Phil. Trans.*, 1906, 205, A, 449) than that previously adopted for the direct measurement of "ionic velocities," we have repeatedly noticed that when certain salts were employed as indicators there was a constant retardation of the margin under observation. It had been previously pointed out (Steele, *Phil. Trans.*, 1901, 198, A, 105) that one of the necessary conditions for a constant margin-velocity was that the indicator should not undergo hydrolysis, and a number of cases of retardation referred to above have been traced to the fact that the indicators in question were somewhat hydrolysed. It occurred to us that the retardation might be capable of quantitative measurement, and might serve as a means of determining, at least approximately, the extent of hydrolysis of the indicator. Our anticipations have been more than realised, as we have found the above principle to be capable of development to an accurate method of measuring hydrolysis which can be carried out with considerable rapidity and in solutions of widely varying concentration.

It has been shown that if solutions of two electrolytes, KA and K_1A , having one ion in common, are superposed, and an electric current is passed through the system, a stable electrolytic margin between the two solutions will result. This margin will move either with or against the current with a definite velocity provided that certain conditions are fulfilled. Of these conditions, the most important is that the specific velocity of the hinder ion is less than that of the ion which it follows. In the accompanying figure (1), if the current is flowing in the direction of the arrows and the non-common ions are the two cations, a stable electrolytic margin of definite velocity will result provided that K_1^+ is specifically slower than K^+ . If this and other conditions are fulfilled, the velocity of the margin is the same as that of the cation K^+ under the particular potential gradient within the solution of the electrolyte KA .*

* For a full discussion of the conditions for a stable margin of constant velocity, see Masson, *Phil. Trans.*, 1899, 192, 331; Steele *loc. cit.*; and Denison and Steele, *loc. cit.*

When, however, the slower or indicator ion is the cation (or anion) of a hydrolysed salt, the case is not quite so simple. Then there exist behind the margin not only K_1^+ cations, but also hydrogen cations, H^+ , and the condition of equilibrium is such that the ratio of the concentrations of the K_1^+ ions to that of the H^+ ions is constant at a given concentration and temperature. Whilst the specific velocity of the K_1^+ ions is less than that of the K^+ ions, the H^+ ions move much faster than either, and by virtue of their greater speed they cross over the boundary between K_1^+ and K^+ . As a result of this overstepping, the system will become divided into three sections, each separated by an ionic margin (Fig. 2).

The uppermost section, *A*, consists of the indicator solution, in which

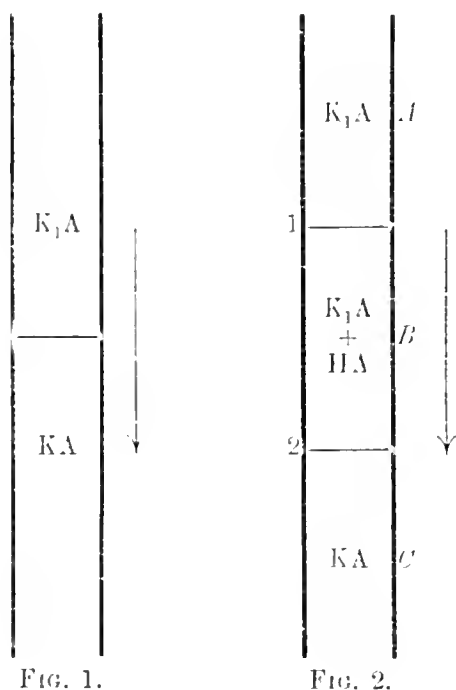


FIG. 1.

FIG. 2.

the concentration of the H^+ ions is constant, and in order to maintain it constant during electrolysis, we must assume that this section is connected with a large reservoir of more concentrated solution, from which the H^+ ions can be replaced as they move away towards the cathode. This section is separated from the next, *B*, by the electrolytic margin (1), which is formed between the ions K_1^+ on the one side and K^+ ions on the other. The section *B* actually consists of a mixture of *KA* and *HA*, the *HA* having been formed by the intrusion of rapidly moving H^+ ions from *A*. In this section also the H^+ ions must have a constant concentration which will

be dependent on the concentration of H^+ ions in *A*. The section *B* extends as far as the foremost H^+ ions, and *B* is thus separated from *C* by a somewhat ill-defined margin (2), which marks the position reached by the front H^+ ions as they travel down the tube. The section *C* contains unchanged *KA*.

Now, the velocity of the margin in Fig. 1 depends upon the potential gradient in the *KA* solution, whereas in Fig. 2 it depends upon the potential gradient in the mixed solution of *KA* and *HA*. But the potential fall is proportional to the resistance, which must be diminished by the intrusion of rapidly moving H^+ ions, and therefore the velocity of the margin (1) must be diminished by hydrolysis in the indicator. Although the measurement of the diminution in velocity of the margin is the most obvious method of applying the foregoing

relations to the measurement of hydrolysis, it is by no means the best or the most accurate method at our disposal. It has been found that by measuring the electrical conductivity of the solution in different parts of the system we have an accurate and simple means of obtaining all the data necessary for calculating the ionic concentration of the hydrogen ions both in front of and behind the margin.

The apparatus employed for the measurement of the conductivity of the solutions during electrolysis is shown diagrammatically in Fig. 3.

Two glass tubes, *A* and *B*, about 2 cm. in diameter, are connected by a narrow tube, *E*, which has a diameter of about 0.6 cm. Each of the tubes *A* and *B* is provided with an electrode vessel, *C* and *D*. The tube *E* is sealed into *A* so as to form a shoulder projecting inwards, and two small platinum electrodes, *b* and *g*, are sealed into the tube about 6 mm. apart, the upper electrode being some 2 cm. from the shoulder. The capillary tube *K* is provided with a bell-shaped enlargement, across the open end of which a membrane of parchment paper can be stretched. The tube *K* slides not too loosely in the rubber cork with which the tube *A* is closed. The tube *B* is similarly closed by a rubber cork carrying the capillary tube *e*. The vessel *D* contains as cathode a piece of lead wire immersed in a paste of lead peroxide and sodium acetate solution. The anode in *C* consists of cadmium amalgam, into which dips a copper wire. In order to

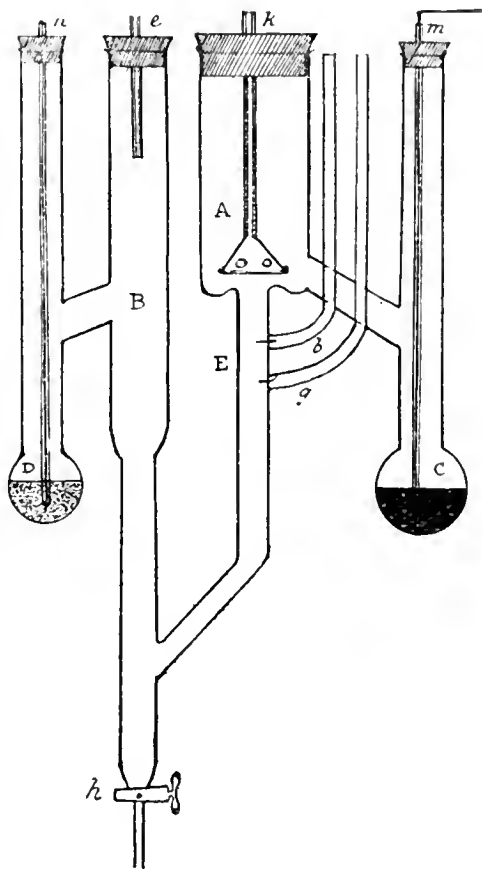


FIG. 3.

carry out an experiment, the tubes *D* and *C* are completely filled, the one with a solution of potassium chloride and the other with a solution of the salt the hydrolysis of which is to be measured. The apparatus is then placed in the thermostat, and a solution of potassium chloride of known strength carefully poured in through *B* until it reaches the level of the shoulder in *A*. When the temperature of the solution is the same as that of the bath, the conductivity is determined by placing the wires from a Wheatstone-Bridge circuit into the mercury contained in the electrode tubes *b* and *g*. The membrane is then brought into

position on the shoulder of *A*, and the current through the apparatus is started by pouring into *B* potassium chloride solution and into *A* the solution to be measured. As a rule, a boundary soon appears in the tube *C*, and the membrane can then be removed, as its object is simply to prevent mixing between indicator and middle solution at the beginning of an experiment. At intervals during the experiment, the conductivity of the solution between the electrodes *b* and *g* is measured. In order to prevent electrolysis taking place at the electrodes *b* and *g*, it is necessary that the circuit through the Wheatstone Bridge and between these electrodes should never be closed at the same time as the main circuit. An arrangement of mercury cups was therefore devised by means of which connection when made in one circuit was broken in the other. During the progress of an experiment, a visible margin appears and advances steadily down the tube *E*. This is margin 1 (Fig. 2). An invisible margin (2), however, moves simultaneously and rapidly in advance of the visible one, and its movement is shown by the increase of the conductivity of the solution in the tube. The conductivity therefore rises steadily, and reaches a maximum when the invisible margin has passed the second platinum electrode. From now onward the conductivity remains constant until the margin (1) reaches the first platinum electrode. This maximum conductivity is that of the mixture of potassium chloride and hydrochloric acid formed by the penetration of the visible electrolytic margin by the rapidly moving H^+ ions, and from the increase in conductivity of the original potassium chloride solution the concentration of the H^+ ions in the mixture of potassium chloride and hydrochloric acid can be calculated. From the moment that the visible margin has passed the first electrode, the conductivity falls rapidly until the margin has passed the second platinum point, when it again becomes constant. This constant value is the conductivity of the indicator solution, and the knowledge of it furnishes us with an easy means of determining the actual concentration of the indicator behind the boundary. This, it should be borne in mind, is not necessarily the same as the concentration of the indicator solution placed in the apparatus, because the concentration of the indicator behind the margin adjusts itself automatically to a value dependent on the concentration of the potassium chloride and the transport numbers of the non-common ions in the potassium chloride and the indicator solution. If, however, by measurements with pure substances we determine the conductivity of solutions of the indicator salt of different concentrations and plot the concentration-conductivity curve, we can read off directly the value of the concentration of the indicator from the last reading in the experiment.

The Calculation of the Concentration of the H⁺ ions in the Solution.

It has been shown (Steele, *loc. cit.*) that if there is no hydrolysis in the indicator the conductivity of the potassium chloride solution, and hence also its concentration, remains constant right up to the margin. In the present experiments this cannot be the case, and, as we shall presently see, the concentration of the K⁺ ions becomes less and that of the Cl⁻ ions greater than the original concentration. This follows from the necessity for equilibrium between the positive and the negative ions present in the system. Every H⁺ ion which crosses the margin displaces a K⁺ ion and partners a Cl⁻ ion which was previously partnered by the displaced K ion.

If κ represents the specific conductivity of the original potassium chloride solution and κ' that of the same solution after the penetration of the H⁺ ions, we have :

$$(1) \quad \kappa = [L_K + L_{Cl}]C,$$

where L_K and L_{Cl} represent the "ionic conductivities" of the K⁺ and Cl⁻ in a solution of potassium chloride containing C mols. per litre.

If a represents the increase in concentration of the Cl⁻ ions and b the diminution in concentration of the K⁺ ions consequent on the entrance of hydrogen ions into the potassium chloride solution, then the concentration of these H⁺ ions must be $(a + b)$, since the solution must remain electrically neutral. If L_H denotes the ionic conductivity of the hydrogen ions at the concentration $(a + b)$ we have :

$$(2) \quad \kappa' = L_K(c - b) + L_{Cl}(c + a) + L_H(a + b)$$

$$\text{or } (2a) \quad \kappa' = [L_K + L_{Cl}]c + L_H[a + b] + aL_{Cl} - bL_K.$$

Subtracting (1) from (2a) we obtain

$$\kappa' - \kappa = (a + b)L_H + aL_{Cl} - bL_K$$

$$\text{or } (a + b) = C_H = \frac{\kappa' - \kappa}{L_H + \frac{a}{a+b}L_{Cl} - \frac{b}{a+b}L_K}.$$

In order to calculate the value of a and b it is necessary to consider the distribution of potential in the portions B and C of the circuit (Fig. 2).

Since the potential gradient in any part of the circuit is proportional to the specific resistance of that part, it is inversely proportional to the specific conductivity. This we have seen to be κ for the section C and κ' for the section B . If p and p' are the corresponding potential gradients, then

$$\frac{p'}{p} = \frac{\kappa}{\kappa'} = \phi \text{ say where } \phi < 1.$$

Let the velocity of the margin (2), that is, of the H^+ ions under the potential gradient p' in B be V , and suppose the velocity of the K^+ ions in C is u , and consequently in B ϕu . Similarly we will assume that the velocities of the Cl^- ions in C and B are respectively v and ϕv . Then the H^+ ions, of which the foremost rank form the boundary (2), overtake and pass the K^+ ions moving in the same direction, and the velocity with which the K^+ ions are overtaken is given by $(V-u)$. However, as soon as the margin (2) overtakes a K^+ ion, the latter is immediately compelled to reduce its velocity from u to ϕu , since behind the margin the potential gradient is only ϕ times that in front of the boundary. Hence the margin (2) as it progresses towards the cathode leaves behind the K^+ ions in B at a rate $(V-\phi u)$, whereas it overtakes those in C with a velocity $(V-u)$. As ϕ is less than 1, the result is that those K^+ ions behind the margin spread themselves over a longer length of tube, that is, their concentration becomes diminished. Denoting distances along the tube by x , we may write

$$\frac{dx}{dt} = \begin{array}{l} \text{velocity with which the margin} \\ \text{overtakes the } K^+ \text{ ions in } C \end{array} = (V-u).$$

$$\frac{dx'}{dt} = \begin{array}{l} \text{velocity with which the margin} \\ \text{leaves behind the } K^+ \text{ ions in } B \end{array} = (V-\phi u).$$

$$\therefore \frac{dx}{dx'} = \frac{V-u}{V-\phi u}.$$

But the volumes occupied by the ions which have moved the distances dx and dx' are respectively sdx and sdx' , where s represents the area of cross section of the measuring tube. Moreover, the concentrations of the K^+ ions on either side of the margin are proportional to the reciprocals of sdx and sdx' .

$$\therefore \frac{\text{Concentration of } K^+ \text{ ions in } B}{\text{Concentration of } K^+ \text{ ions in } C} = \frac{sdx}{sdx'} = \frac{V-u}{V-\phi u}.$$

Hence

$$\text{Concentration of } K^+ \text{ ions in } B = C_B = c \left(\frac{V-u}{V-\phi u} \right).$$

If we denote by N the ratio of the mobilities of H^+ and K^+ , then $\frac{V}{u} = N$, and $C_B = c \left(\frac{N-1}{N-\phi} \right)$.

Therefore the loss of concentration of K^+ ions in $B = c - c \left(\frac{N-1}{N-\phi} \right)$
or $b = c \left(\frac{1-\phi}{N-\phi} \right)$.

Similarly, by considering the motion of the Cl^- ions on either side of the margin (2), we have :

Velocity with which the Cl' ions in *C* approach the margin (2) = $V + v$.

Velocity with which the Cl' ions in *B* recede from the margin = $V + \phi v$.

Thus the Cl' ions in *B* cannot move away from the margin as quickly as those in *C* approach it, and the result is an increase in the concentration of Cl' ions in *B*.

As before :

$$\frac{\text{Concentration of Cl' ions in } B}{\text{Concentration of Cl' ions in } C} = \frac{V + v}{V + \phi v}.$$

$$\therefore \text{Concentration of Cl' ions in } B = C''_B = c \left(\frac{V + v}{V + \phi v} \right).$$

$$\text{If the ratio } \frac{V}{v} = N' \text{ then } C''_B = c \left(\frac{N' + 1}{N' + \phi} \right).$$

$$\therefore \text{Increase of Cl' ions in } B = (C''_B - C) = c \left\{ \left(\frac{N' + 1}{N' + \phi} \right) - 1 \right\} = c \left(\frac{1 - \phi}{N' + \phi} \right).$$

$$\therefore a = c \left(\frac{1 - \phi}{N' + \phi} \right).$$

$$\text{Hence } (a + b) = C''_B = c \left\{ \frac{1 - \phi}{N' + \phi} + \frac{1 - \phi}{N - \phi} \right\} = \frac{c(1 - \phi)(N + N')}{(N' + \phi)(N - \phi)}.$$

$$\therefore \frac{a}{a + b} = \frac{N - \phi}{N + N'} \text{ and } \frac{b}{a + b} = \frac{N' + \phi}{N + N'}.$$

We are now able to express the concentration of the H' ions in the portion *B* of the tube, and it only remains to calculate from this the concentration of the H' ions in the indicator solution. This can be done by a similar calculation to the above, whereby the visible boundary (1) is considered. If κ'' and p'' represent the specific conductivity and potential gradient respectively in *A*, then we have the relation :

$$\frac{p'' \text{ in } A}{p' \text{ in } B} = \frac{\kappa' \text{ in } B}{\kappa'' \text{ in } A} = \pi.$$

The velocity of the margin (1) is that of the K' ion under the potential gradient p' . Let this velocity be u and the velocity of the H' ions in *A* be V' , the H' ions in *B* having of course a velocity V as previously stated. Then $V' = \pi V$, or if $\frac{V'}{u} = N$, $V = \pi Nu$.

In exactly the same way as before we obtain the relation :

$$\frac{\text{Velocity with which the H' ions in } A \text{ approach margin (1)}}{\text{Velocity with which the H' ions in } B \text{ leave margin behind}} =$$

$$\frac{V' - u}{V - u} = \frac{N\pi - 1}{N - 1}.$$

Hence

$$\frac{\text{Concentration of H}^+ \text{ ions in } B}{\text{Concentration of H}^+ \text{ ions in } A} = \frac{N\pi - 1}{N - 1}.$$

$$\therefore \text{Concentration of H}^+ \text{ ions in } A = \frac{N - 1}{N\pi - 1} [a + b].$$

Combining this result with that previously obtained for $(a + b)$ we have:

Concentration of H⁺ in indicator =

$$\frac{N - 1}{N\pi - 1} \left\{ L_{\text{H}} + \left(\frac{N - \phi}{N + N'} \right) L_{\text{Cl}} - \left(\frac{N' + \phi}{N + N'} \right) L_{\text{K}} \right\}.$$

From the measurement of the conductivity of the three portions, C, B, and A, as they successively come between the electrodes during the course of an experiment, we obtain κ , κ' , and κ'' .

$$\text{Then } \frac{\kappa'}{\kappa''} = \pi, \quad \frac{\kappa'}{\kappa} = \phi.$$

N and N' are obtained from conductivity measurements or by direct measurement (see Denison and Steele, *loc. cit.*). The values taken here were those found by Denison and Steele, and are given below:

$$N' = \frac{L_{\text{H}}}{L_{\text{Cl}}}, \quad N = \frac{L_{\text{H}}}{L_{\text{K}}}.$$

Dilution.	At 18°.			At 25°.		
	10.	50.	100.	10.	50.	100.
L_{Cl}	56.7	69.8	62.0	65.1	69.8	71.5
L_{K}	55.2	59.2	60.3	63.2	67.9	69.6
N	5.68	5.3	5.2	5.19	4.83	4.72
N'	5.52	5.14	5.65	5.04	4.70	4.59

It has been assumed that the mobility of the H⁺ remained the same in the different experiments at the same temperature. This must be very nearly so since the solutions of potassium chloride are dilute, and the concentration of the H⁺ ions in the various experiments was of the same order of magnitude (approximately 0.001 normal). The values assumed for L_{H} were, at 18°, 313, and at 25°, 328. Should these values prove later to be not quite correct, the method would not thereby lose in value, and the actual figures now obtained would only be slightly in error.

As the object of the present research was to test thoroughly the method, three salts only have been submitted to measurement, namely, the hydrochlorides of aniline, and of *ortho*- and *para*-toluidine. The measurements were carried out at temperatures of 18° and 25° and at concentrations of 0.1, 0.02, and 0.01 normal.

A few of the earlier measurements were made with salts which had been prepared from an ordinary sample of the organic base. The method proved itself, however, sufficiently sensitive to indicate the presence of impurities in these salts, and this was afterwards confirmed by direct experiment. The salts were therefore prepared by dissolving a quantity of the carefully fractionated free base in ether, and passing hydrochloric acid gas into the solution. The precipitated hydrochloride was washed with ether and then crystallised from three to seven times from alcohol until the aqueous solution had attained a constant conductivity.

The conductivity of the salt was then measured at dilutions varying from $v=8$ to $v=200$, and the results were plotted on a specific conductivity—dilution curve. These curves were afterwards used for the determination of the concentration of the indicator solution of which the hydrolysis was measured. The following are the values obtained for the conductivities of the pure salts.

Aniline Hydrochloride.

Salt.	At 18°.			At 25°.		
	Dilution V , that is, no. of litres containing 1 gram-mol.	Specific con- ductivity. κ .	Molecular con- ductivity. $\mu = \kappa V \times 10^3$.	Dilution V , that is, no. of litres containing 1 gram-mol.	Specific con- ductivity. κ .	Molecular con- ductivity. $\mu = \kappa V \times 10^3$.
Aniline hydrochloride	8	0.00976	78.1	8	0.01127	90.16
	16	0.00529	84.7	16	0.00621	99.4
	32	0.00284	90.9	32	0.003318	106.2
	40	0.002295	91.9	40	0.002696	107.8
	64	0.001505	96.3	64	0.001792	114.6
	80	0.001231	98.5	80	0.001451	116.0
	128	0.0008075	103.2	128	0.000952	121.7
	160	0.0006515	104.2	160	0.000765	122.3
	200	0.0005295	105.9	200	0.000633	126.6
<i>o</i> -Toluidine hydrochloride	8	0.00945	75.6	8	0.01103	88.24
	16	0.00516	82.6	16	0.00609	97.5
	32	0.00279	89.4	32	0.00330	105.6
	64	0.001497	95.9	64	0.001770	113.2
	80	0.001234	98.8	80	0.001475	118.0
	128	0.000800	102.4	128	0.000945	120.9
	160	0.000658	105.2	160	0.000781	124.8
	200	0.000532	106.4	200	0.000655	131.0
At 24.8°.						
<i>p</i> -Toluidine hydrochloride	16	0.00493	78.9	16	0.00584	93.5
	32	0.00266	85.2	32	0.00311	99.6
	64	0.001405	90.0	64	0.001648	105.3
	80	0.001137	91.0	80	0.001325	106.0
	128	0.000745	95.4	128	0.000859	110.0
	160	0.000598	95.9	160	0.000795	112.7
	200	0.000485	97.0	200	0.000575	115.0

Results of Hydrolysis Measurements.

	At 18°.			At 25°.			<i>q.</i>
	<i>V</i> .	<i>x</i> per cent.	$K/10^3$.	<i>V</i> .	<i>x</i> per cent.	$K/10^3$.	
<i>o</i> -Toluidine	100	1.97	47.5	18.3	2.49	28.8	11,000 cals.
hydrochloride	92	4.53	43.3	91	5.10	29.5	
	88	4.40	44.3	155	7.15	28.2	
	175	5.75	49.9	172	7.10	31.0	
	Mean $K/10^3$ at 18° = 46.0			Mean $K/10^3$ at 25° = 29.6			
<i>p</i> -Toluidine	17.6	0.85	242	17.4	0.94	195	7900 cals.
hydrochloride	18	0.84	253	88	2.12	191	
	82	1.82	243	90	2.17	187	
	89	1.82	263	165	3.02	176	
	161	2.39	276	166	2.97	183	
	Mean $K/10^3$ at 18° = 256			Mean $K/10^3$ at 25° = 186			
Aniline	17.6	1.64	64.6	17.9	1.98	44.3	8700 cals.
hydrochloride	82	3.63	60.9	18.2	1.99	44.8	
	167	5.16	59.6	79	4.12	44.5	
	175	5.13	63.3	81	4.37	40.5	
	Mean $K/10^3$ at 18° = 61.9			84	4.39	41.8	
				157	5.60	46.6	
				167	6.08	42.6	
				Mean $K/10^3$ at 25° = 43.6			

In the above table, the results of the experiments at 18° and 25° are placed side by side. In column I are the dilutions of the solutions of the indicators in litres, the numbers under *V* represent the number of litres of the indicator solution containing one gram-molecule of the hydrochloride. These solutions are hydrolysed or split up by the water into acid and base to a degree of *x* per cent. The values of *x* are given in the second column. In the third column are placed the values of $\frac{K}{1000}$, *K* being the hydrolysis constant which is given

by the ratio $\frac{\text{per cent. unhydrolysed salt} \times \text{dilution } (V)}{\text{per cent. free acid} \times \text{per cent. free base}}$.

The concentrations of free acid and free base formed by hydrolysis are of course identical.

In order to render more evident the method of arriving at the above figures, it will be perhaps not out of place to work out completely one set of experimental figures. As an example we take an experiment with aniline hydrochloride acting as indicator to an approximately 0.02 normal solution of potassium chloride at 25°. The following figures were obtained:

Specific conductivity of potassium chloride alone: $\kappa = 0.002560 \text{ ohm}^{-1}$.

Maximum specific conductivity of potassium chloride after penetration of H⁺ ions: $\kappa' = 0.002960 \text{ ohm}^{-1}$.

$$\therefore \kappa' - \kappa = 0.000400 \text{ ohm}^{-1}.$$

Specific conductivity of indicator solution behind the margin = $0.001385 \text{ ohm}^{-1}$, which corresponds on the concentration--conductivity curve to a concentration of $\frac{1}{84.4} \frac{\text{gram-mols.}}{\text{litre}}$, that is, to a dilution of 84.4.

$$\text{Now } \phi = \frac{\kappa}{\kappa'} = 0.86, \quad \pi = \frac{2960}{138.5} = 2.14.$$

$$N = \frac{L_{\text{H}^+}}{L_{\text{K}^+}} = \frac{328}{67.9} = 4.83, \quad N' = \frac{L_{\text{H}^+}}{L_{\text{C}}} = \frac{328}{69.8} = 4.70.$$

$$\therefore \frac{N\pi - 1}{N - 1} = 2.43.$$

Hence, from the formula previously deduced, the concentration of the H⁺ ions in the potassium chloride solution is

$$\begin{aligned} & \frac{0.000400}{328 + \frac{(4.83 - 0.86)69.8}{9.53} - \frac{(4.70 + 0.86)67.9}{9.53}} \\ & = \frac{0.000400}{316}. \end{aligned}$$

therefore the concentration of H⁺ ions in indicator solution of dilution

$$84.4 = \frac{0.000400}{316 \times 2.43}.$$

Whence hydrolysis $x = \frac{C_{\text{H}^+} \times 100}{\text{Concentration salt in gram-mols. per c.c.}}$

$$= \frac{400 \times 10^{-10} \times 84.4 \times 10^3 \times 100}{316 \times 2.43} = 4.39 \text{ per cent.}$$

$$\text{Therefore hydrolysis constant } K = \frac{95.6 \times 8440}{[4.39]^2} = \underline{41.8 \times 10^3}.$$

This hydrolysis constant K gives us the number of times that the free base (in this case aniline) is "stronger" than water, that is, $K = \frac{Kb}{Kw}$, where Kb and Kw represent the affinity constants of the base and of water respectively. Accepting the value 1.2×10^{-14} for Kw we have for the affinity constant of

$$\left. \begin{array}{lll} \text{Aniline.....} & 1.2 \times 10^{-14} \times 43.6 \times 10^3 = 5.2 \times 10^{-10} \\ \text{para-Toluidine...} & 1.2 \times 10^{-14} \times 186 \times 10^3 = 2.2 \times 10^{-10} \\ \text{ortho-Toluidine..} & 1.2 \times 10^{-14} \times 29.6 \times 10^3 = 3.5 \times 10^{-10} \end{array} \right\} \text{at } 25^\circ.$$

The corresponding values for 18° are :

	<i>K</i> b.
Aniline.....	7.4×10^{-10}
<i>para</i> -Toluidine.....	3.1×10^{-9}
<i>ortho</i> -Toluidine	5.5×10^{-10}

Thus we see that the order of "strength" of these bases is *para*-toluidine, aniline, *ortho*-toluidine. This corresponds, of course, to the degree of hydrolysis being greatest in *ortho*-toluidine and least in *para*-toluidine.

A glance at the previous table shows that the values obtained for the hydrolysis constant *K* are fairly concordant. Absolute constancy is, of course, not to be expected when one bears in mind the number of different quantities which have to be determined before the degree of hydrolysis *x* can be calculated, and that in the calculation of *K* there occurs the term *x*². Hence, any accumulated error in the determination of *x* becomes multiplied in *K*, and it therefore says much for the accuracy of the method and for the correctness of the theory that a "constant" for *K* has been obtained at all. It is interesting to compare the present method with others which have been employed for the measurement of hydrolysis. It need scarcely be noted that the whole difficulty about such measurements lies in the fact that the determinations of concentrations must be carried out in such a manner that the state of equilibrium between the different component parts of the system is not altered. In such cases as we have considered, the problem becomes that of the measurement of the free acid produced by the hydrolysis. The concentration of this acid is so small that it must be practically all dissociated, and hence any method of measuring the concentration of the H⁺ ions will serve our purpose. Methods depending upon catalysis, such as the "inversion" of cane sugar or the catalysis of methyl acetate, are somewhat unsuitable for the determination of the concentration of H⁺ ions in systems which contain a complicated equilibrium, because we know that these methods are much affected by the presence of even simple neutral salts. Moreover, the velocity of catalysis is small, and so measurements of small degrees of hydrolysis at the ordinary temperature take an inordinate time.* Yet it is just the hydrolysis data for the ordinary temperature which give us so much useful information. The best method for the measurement of acid hydrolysis, as regards both ease of manipulation and accuracy of results obtained, is that suggested by Walker and Bredig. This method consists in the measurement of the electrical conductivity of,

* The same objections cannot be raised against the method of Shields, which, however, refers to OH⁻ ions.

firstly, the hydrolysed salt solution, and, secondly, of the same solution with the addition of an excess of the base contained in the salt. This addition almost completely inhibits the hydrolysis, so that the second reading gives the true electrical conductivity of the salt in question *plus* a negligible amount due to the conductivity of the weak base; the latter being in the presence of excess of its ionised salt, and therefore practically undissociated. Thus, if M_v is the actually observed molecular conductivity of a solution of aniline hydrochloride, M_v is made up of the conductivity of $(1-x)$ mols. of aniline hydrochloride and x mols. of free hydrochloric acid. If μ_v represents the true molecular conductivity of aniline hydrochloride at a dilution v determined in the presence of excess of aniline, then $M_v = (1-x)\mu_v + x\mu_{\text{HCl}}$ or

$$x = \frac{M_v - \mu_v}{\mu_{\text{HCl}} - \mu_v};$$

μ_{HCl} represents the molecular conductivity of hydrochloric acid at a dilution which is practically infinite for small degrees of hydrolysis. For the value of μ_{HCl} , Bredig took 383 at 25°, probably in Siemens units, which means 0.406 in ohm^{-1} . Taking the transport number of chlorine in hydrochloric acid as 0.17, then $l_{\text{H}} = 406 \times 0.83 = 337$ and $l_{\text{Cl}} = 406 \times 0.17 = 69$. It is, however, probable that these numbers are rather high for the actual ionic conductivities in the presence of a large excess of aniline hydrochloride. This is practically the only uncertainty of the method, and even then it amounts to perhaps not more than a few units or a percentage error in l_{H} of 1—2 per cent. By this method, Bredig's determinations of hydrolysis "constants" were the best which had been obtained for acid hydrolysis; in fact, many of the investigations by the catalysis methods failed to give any hydrolysis "constant" at all, especially where the degree of hydrolysis was small.

Bredig's method has, however, limitations: the amount of the free base added must be sufficient to inhibit the hydrolysis sufficiently without its own conductivity becoming appreciable. This is not always possible, because the base may not be sufficiently soluble or its conductivity may be too great to be neglected. The present method will no doubt prove useful in cases where the older one fails. The principle of the method is really a device for separating the H^+ ions and measuring their concentration by noting the increase of conductivity caused by them. Bredig's method consists in destroying these same H^+ ions and measuring their concentration by the consequent loss in conductivity. Hence the two methods, although starting from quite different standpoints, are really very similar in the end, and both require for the calculation the value of the ionic conductivity of the H^+ ions at their concentration in the experiment. Seeing that the

degrees of hydrolysis of those salts measured by us did not differ very much, it was assumed that the concentrations of the H^+ ions in the different experiments were sufficiently nearly equal to warrant the assumption of a constant ionic conductivity for the H^+ ion throughout; that is, of course, at the same temperature. The values taken were 313 at 18° and 328 at 25° .

The constants of hydrolysis K for the hydrochlorides of aniline, and *o*- and *p*-toluidine were found by Bredig to have the values at 25° as follows:

<i>p</i> -Toluidine	$K \times 10^3 = 132$
Aniline	$K \times 10^3 = 41$
<i>o</i> -Toluidine	$K \times 10^3 = 29$

which accord very well with the values found by us. In the case of aniline and *o*-toluidine, the values of K found by the two methods are so near that the apparent difference vanishes when one works out from the "constant" the actual degrees of hydrolysis corresponding to any given concentration. As regards *p*-toluidine, there is, it is true, a somewhat greater difference in the value of K as determined by the two methods. Bredig gives 132×10^3 , whereas we find 186×10^3 . Still one obtains almost the same percentage hydrolysis in a given case whichever "constant" be taken. For instance, for $1/32N$ (*para*-toluidine hydrochloride), Bredig's constant gives for the degree of hydrolysis 1.55 per cent., whereas ours yields 1.33 per cent. It must be borne in mind that the measurements of such small amounts of hydrolysis involves a considerable percentage experimental error, and, as previously explained, these errors are largely magnified in K .

As a check on our work, we have applied van't Hoff's formula $\frac{d}{dT} \log K = \frac{q}{2T^2}$ to our values for K at the two temperatures. Assuming that q , the heat evolved by the "neutralisation" of a gram-mol. of base with hydrochloric acid, remains constant, we have, on integration:

$$\log \frac{K_1}{K_2} = \frac{q}{2} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

For our temperatures 18° and 25° , this becomes:

$$2.30 \log \frac{K_{18}}{K_{25}} = \frac{q}{2} \left(\frac{1}{291} - \frac{1}{298} \right),$$

whence q is evaluated.

Owing to a somewhat large percentage error in K being easily possible, one cannot expect too good an agreement of the value of q obtained in this way with the value obtained calorimetrically. However, as is seen from Table II, the agreement in the case of aniline

and *p*-toluidine is sufficiently close, which proves that although the absolute values of the hydrolysis constants at the two temperatures may be slightly inaccurate, yet their ratio must have very nearly the true value.

Enough has perhaps been said to substantiate the claims of the present method to be one of the most accurate and convenient means of determining the degree of hydrolysis of salts. The method can, moreover, be extended to determine the concentration of given ions in complex mixtures, provided that these ions fulfil the conditions on which the method depends. These experiments are being extended, and it is hoped to measure the hydrolysis of many salts both organic and inorganic.

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CV.—*The Solubility of Triphenylmethane in Organic Liquids with which it forms Crystalline Compounds.*

By HAROLD HARTLEY, M.A., Fellow of Balliol College, and
NOEL GARROD THOMAS, Brakenbury Scholar, Balliol College.

KEKULÉ and Franchimont (*Ber.*, 1872, 5, 967), when they first prepared triphenylmethane, noticed that it crystallised from benzene with one molecule of benzene of crystallisation, and Anschütz (*Annalen*, 1886, 235, 208) found that the compound lost 24.22 per cent. of its weight when heated to 100°, the theoretical loss for a substance of formula $\text{CH}(\text{Ph})_3 \cdot \text{C}_6\text{H}_6$ being 25.36 per cent.

Liebermann (*Ber.*, 1893, 26, 853) crystallised triphenylmethane from thiophen and obtained crystals with thiophen of crystallisation, which was rapidly lost on standing. The crystals lost 24.54 per cent. of their weight when heated to 100°, the theoretical loss for $\text{CH}(\text{Ph})_3 \cdot \text{C}_4\text{H}_4\text{S}$ being 25.61 per cent.

Lehmann (*Zeit. Kryst. Min.*, 1881, 5, 472), who studied the crystallisation of triphenylmethane from aniline microscopically, stated that it crystallised in two forms belonging to the rhombohedral and monoclinic systems, which differ in the amount of aniline of crystallisation, but he made no attempt to estimate this amount in either case. Hintze (*Zeit. Kryst. Min.*, 1884, 9, 545) made some measurements on "weathered" crystals from benzene solution and pointed out that if the crystals containing aniline resembled those containing benzene, Lehmann's two forms were probably identical, their difference in

appearance under the microscope being due to a different development of the basal plane.

Linebarger (*Amer. Chem. J.*, 1893, 15, 45) was the first to study the solubility of triphenylmethane in benzene, his determinations being made by the ordinary method. As, however, he heated the triphenylmethane to 200° to get rid of the last traces of benzene, and at this temperature the substance itself is appreciably volatile, his results were necessarily inaccurate; they differ from the later determinations of Kuriloff (*Zeit. physikal. Chem.*, 1897, 23, 547), which agree closely with those found by the authors, using a slightly modified form of his method.

The first object of the present work was to determine if there were any other solvents which form crystalline compounds with triphenylmethane; only pyrrole was found to do so. Solutions in mesitylene, *o*-, *m*-, and *p*-xylene, toluene, pyridine, piperidine, nitrobenzene, chlorotoluene, benzyl alcohol, quinoline, bromobenzene, chlorobenzene, methylbenzoate, phenyl acetate, propyl alcohol, acetone, chloroform, ethylene dibromide, alcohol, and ether all gave orthorhombic crystals of pure triphenylmethane.

A microscopic study has been made of the crystals containing benzene, thiophen, pyrrole, and aniline of crystallisation, all of which decompose rapidly on being removed from the solution in which they have grown, the faces becoming dull and giving very poor reflections on the goniometer. We hope soon to measure them while growing in a solution by means of Prof. Miers' inverted goniometer.

The solubility of triphenylmethane in the four liquids above mentioned has been determined, and, for purposes of comparison with a case in which no compound with the solvent existed, a set of determinations was also made in pyridine.

Besides the solubility determinations, a series of observations was made at the suggestion of Prof. Miers to see at what degree of supersaturation solutions of triphenylmethane would crystallise spontaneously, after they had been completely freed from crystal nuclei. This was done by heating them considerably above the temperature at which all the solid in contact with the solution had dissolved, and then cooling until the crystallisation occurred. Spontaneous crystallisation in such a case has been found to occur at a definite temperature, thus fixing the limit of the "metastable state" in which, although supersaturated, a solution cannot crystallise without the addition of a crystal particle (Ostwald, *Lehrbuch der Allgemeinen Chemie*, 2, 773).

EXPERIMENTAL.

Preparation of Materials.

The triphenylmethane used was prepared by the ordinary method from Kahlbaum's chloroform and benzene with freshly made aluminium chloride. It was recrystallised twice from benzene and at least twelve times from alcohol until it gave a constant m. p. of 93.2° (corr.); this is slightly higher than the number given by Kuriloff (92°). The solvents used were all obtained from Kahlbaum or Merck, and carefully redistilled just before use.

Method of Determining the Solubility.

The ordinary methods for determining solubilities being difficult to use owing (1) to the volatility of benzene, thiophen, and pyrrole; (2) to the difficulty of estimating the relative amounts of aniline and triphenylmethane in a mixture of the two, and (3) to the small amounts of substance available, we resorted to a modification of the method used by Kuriloff (*loc. cit.*).

The latter heated sealed tubes containing known quantities of triphenylmethane and benzene in a water-bath with constant shaking until the last crystals just dissolved. In this way the temperature of saturation was found for solutions of known composition. It is rather hard to say when the last crystals disappear, as they dissolve very slowly in a solution which is nearly saturated. When, on the other hand, we contrived by successive cooling and warming that there should be in the tube only one or two small crystals at a temperature near that of saturation, it was easy, by watching the small crystals with a lens while the temperature of the bath was varied, to find two temperatures differing by 0.4° to 0.5° , at the lower of which the crystals were growing with sharp edges, whilst at the higher temperature the rounded edges and faces showed that they were dissolving. The mean of these two temperatures may be taken as the temperature of saturation without introducing a large error. The results obtained in successive determinations are quite concordant and the method has several advantages, as it is quick, requires very little substance, and may be used for any volatile solvent; the fact that it necessitates the close study of the crystals with which the solution is in equilibrium leaves no ambiguity as to their nature. The most useful form of tube was made by blowing a bulb at one end of a short piece of quill tubing and making a small constriction in the middle. After careful drying the tube is weighed, some of the solid is introduced, and it is weighed again; then the required quantity of liquid is added from a small pipette, and, after a third

weighing, the tube is sealed at the constriction. The open end is closed by a small cap during the weighing and sealing to avoid loss by evaporation, and contact with the hand is carefully avoided for the same reason. The tubes were heated in a large beaker of water, jacketed with felt, and stirred by means of a hot air engine. By adjusting the size of the Bunsen flame, the temperature of the water could be kept constant for as long as was necessary.

In order to determine the temperature of spontaneous crystallisation, the tube is heated in a large beaker of water at 10° above the saturation temperature to destroy all traces of crystal nuclei, and it is then allowed to cool slowly with constant shaking until crystals appear.

The spontaneous production of crystals never occurs until a temperature is reached at which the solution is considerably supersaturated, and then many small crystals suddenly make their appearance. At least two determinations were made with each tube; as a rule they agreed within 1° , which was fairly satisfactory considering the nature of the phenomenon, and the extent to which it would be influenced by such factors as the rate of cooling. The time taken for cooling in most of the experiments was between half an hour and an hour. A curve may be plotted from the results showing the concentration at which the spontaneous crystallisation of a solution at any given temperature occurs. In the region between the solubility curve and this second curve, for which Prof. Miers has suggested the name "supersolubility curve," supersaturated solutions can exist without crystallising until a crystal nucleus is introduced.

Triphenylmethane and Benzene.

The results of the determination of solubility and of the temperature at which spontaneous crystallisation takes place are given in the table on p. 1017, and are shown graphically in Fig. 1 (p. 1018), where the ordinates represent molecular percentages and the abscissæ temperatures.

The solubility curve consists of two parts, of which *AB* represents the solubility of triphenylmethane in benzene, and *BCD* the solubility of the compound $\text{CH}(\text{Ph})_3 \cdot \text{C}_6\text{H}_6$, *C* being its melting point, which is depressed by the addition of benzene or of triphenylmethane. The point in which the two cut (*B*) is a eutectic point for the compound and pure triphenylmethane. The large curvature of the retroflex portions of the lower curve indicates that the compound is almost entirely dissociated in the solution (Stortenbecker, *Zeit. physikal Chem.*, 1892, 10, 194). It will be seen that the "supersolubility curve" also consists of two parts which run, roughly speaking, parallel to the two

Solubility of Triphenylmethane in Benzene.

Gram of triphenylmethane.	Gram of benzene.	Percent-age of triphenylmethane.	Molecular percent-age of triphenylmethane.	Saturation temperature.	Form of crystals.	Limit of metastable region.	Form of crystals.
0.5682	0.0254	95.7	87.8	86.6°	N	67.3°, 65.5°	N
0.5392	0.0400	93.1	81.3	82.3	N	58.5, 58.4	N
0.5417	0.0568	90.5	75.3	78.8	N	62.6, 62.4	RN
0.6850	0.0846	89.0	72.2	76.0	N	63.8, 63.8	RN
0.4969	0.0714	87.5	69.1	74.6	N	65.4, 61.5	RN
0.4822	0.0911	84.1	62.8	76.2	R	66.8, 66.2	R
0.6157	0.1523	80.2	56.4	77.5	R	69.2, 68.7	R
0.3848	0.1198	76.3	50.7	77.9	R	69.3, 68.7	R
0.4222	0.2043	67.4	39.7	77.1	R	70.3, 69.8	R
0.2992	0.2212	57.5	30.2	73.8	R	67.6, 67.2	R
0.2357	0.3617	38.9	17.2	65.6	R	58.3, 58.0	R
0.1600	0.5064	24.0	8.8	49.4	R	42.1, 41.7	R
0.0636	0.4395	12.6	4.4	33.0	R	28.0, 27.5	R

N denotes monoclinic needles (CHPh_3).

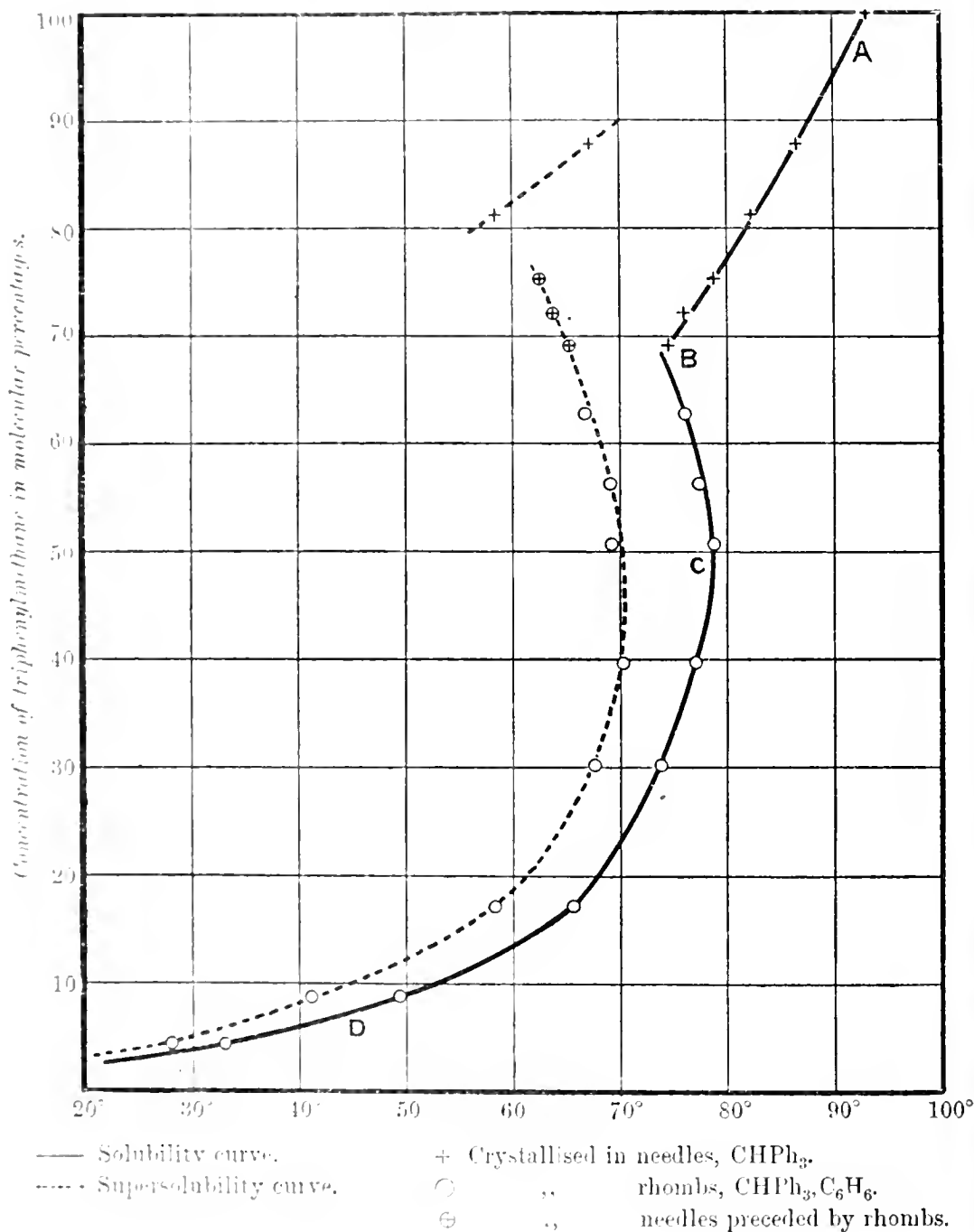
R „ rhombs ($\text{CHPh}_3 \cdot \text{C}_6\text{H}_6$).

parts of the solubility curve. The range of the "metastable region" is about 20° for solutions which deposit crystals of pure triphenylmethane and about 7° for those which deposit crystals containing benzene of crystallisation. Thus, for the formation of crystals of the compound, a smaller degree of supersaturation is needed than is the case with the pure substance; in consequence of this, solutions containing from 70—80 mols. per cent. of triphenylmethane, which are normally in equilibrium with crystals of the pure substance, if freed from crystal nuclei and cooled, deposit crystals of the compound while still within the metastable region of the pure substance. For instance, a solution containing 75 mols. per cent. of triphenylmethane, when cooled to 63° , deposits rhombohedral crystals of the compound, and these have the property of starting the crystallisation of orthorhombic needles of triphenylmethane when placed in solutions which are in the metastable condition as regards the latter substance. The orthorhombic needles grow on the rhombohedra, so that the vertical axes of both are parallel as in Fig. 2. The edges of the needles are usually curved owing to the rapidity of their growth in its initial stages. The second crystallisation takes place very rapidly after the first, and the sequence is sometimes rather hard to observe. It will be seen that in the cases where this occurs (marked RN on the table and indicated on the diagram by \oplus) the temperatures of crystallisation lie on the continuation of the curve which represents the limit of supersaturation for the compound.

The Compound of Triphenylmethane and Benzene.

The composition of this body was shown by Anschütz to be $\text{CH}(\text{Ph})_3 \cdot \text{C}_6\text{H}_6$. Hintze measured some of the "weathered" crystals

FIG. 1. Solubility and supersolubility curves of triphenylmethane in benzene.



which had lost their benzene of crystallisation and found them to be rhombohedra with a rhombohedral angle $110^\circ 13'$ and $a:c=1.5565$. We have studied a large number of crystallisations under the micro-

scope; the most frequent habits of the crystals are (1) a simple rhombohedron, (2) a combination of rhombohedron and small basal plane (Fig. 3), (3) a combination of rhombohedron and basal plane equally developed (Fig. 4), and (4) the same combination with the basal plane predominating (Fig. 5).

The crystals have a high refractive index and are strongly birefringent. Viewed in convergent light in a direction perpendicular to the basal plane, they show a uniaxial interference figure of negative character, which confirms the other evidences as to their symmetry. No distinct etching figures could be obtained on the rhombohedron faces,



FIG. 2.

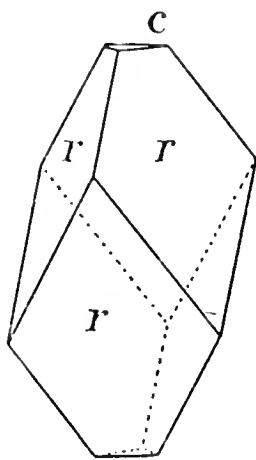


FIG. 3.

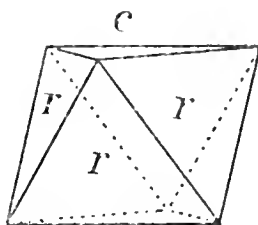


FIG. 4.

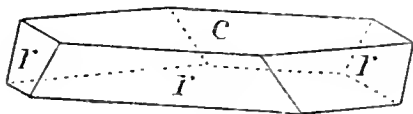


FIG. 5.

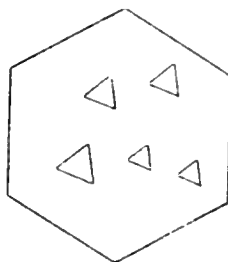


FIG. 6.

but in the initial stage of solution the basal plane was pitted by small triangular depressions arranged unsymmetrically with respect to its edges as shown in Fig. 6. The crystals thus possess an axis of threefold symmetry, but no plane of symmetry. There is no evidence of hemimorphism, as both ends of the crystals are equally developed, and behave in the same way in starting the crystallisation of orthorhombic needles of triphenylmethane as mentioned above. The latter crystals are hemimorphic, and the two ends grow at very different speeds, but when their crystallisation is started by a rhombohedral crystal of the compound, they grow outwards from both apices of the rhombohedron with faster-growing ends directed outwards from the

crystal in each case, showing that there is no difference between the faces (111) and $(\bar{1}\bar{1}\bar{1})$.

The crystals of the compound thus possess an axis of threefold symmetry and a centre of symmetry, and belong to the diopside class.

A number of measurements of the angle between the two edges of a rhombohedron face showed that this is approximately 60° ; the rhombohedron angle $(100):(010)$ calculated from this value is $109^\circ 28'$, which differs slightly from Hintze's measurement on a "weathered" crystal ($110^\circ 13'$). In a rhombohedral crystal with the angle $(100):(010) = 109^\circ 28'$, both the angles $(100):(111)$ and $(100):(010)$ have the value $70^\circ 32'$ (the octahedron angle), so that a crystal with the forms $\{111\}$ and $\{100\}$ equally developed is indistinguishable geometrically from a regular octahedron.

The effect of this curious symmetry of angle is seen in the present case in the form of the interpenetrant twins and triplets which frequently occur. The crystals twin about an axis which is parallel to a rhombohedron edge, giving rise to interpenetrant twins of the form seen in Fig. 7, where the shading indicates the relative positions of the two individuals and the extent to which they overlap. The letters $r' c'$, $r'' c''$ show which faces belong to each individual. The extinction directions of the two parts of the twin make an angle of 60° with one another, and, as would be expected, no re-entrant angle is visible under the microscope where the faces of the two individuals meet.

Still more frequent is the formation of triplets where the three individuals interpenetrate regularly, as in Fig. 8; sometimes the basal planes $\{111\}$ are developed sufficiently to give rise to the form shown in Fig. 9. In this case the crystal appears at first sight to be a simple combination of the forms $\{111\}$ and $\{100\}$, as in Fig. 5, but optical examination shows that the apparent basal plane is composed of the rhombohedral faces of three individuals, as is evident from the interference figures seen through the six sections of the face, which are shown in Fig. 9. The six small faces bounding the hexagonal plane are the basal planes of the three individuals. Here, again, the regular formation without visible re-entrant angles shows that the rhombohedron angle of the single crystals must be approximately $109^\circ 28'$. Figs. 7, 8, and 9 are plans representing the crystals just as they are seen through a microscope.

When simple crystals of the type represented in Fig. 5 start to grow in strongly supersaturated solutions, they give rise to skeletal forms in accordance with Lehmann's theory that the latter are due to a difference in the rate of supply of material for crystallisation at different points of a growing crystal. Suppose that a crystal is growing with its basal plane resting on the microscope slide, it grows

laterally by the deposition of substance on the six rhombohedron faces. Now, of the six rhombohedron faces, three have the edge which extends furthest into the solution practically in contact with the glass, and three have the corresponding edge in the middle of the drop of solution. The latter must therefore receive a more rapid supply of the excess of dissolved substance, and will grow faster, and these three faces, having once pushed themselves further into the solution

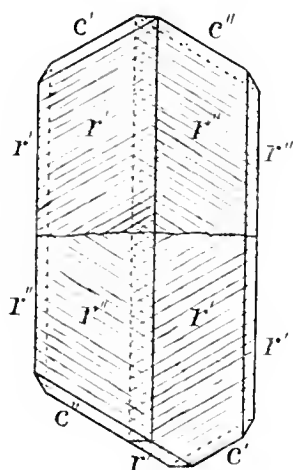


FIG. 7.

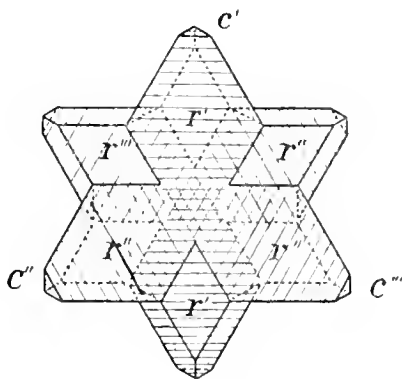


FIG. 8.

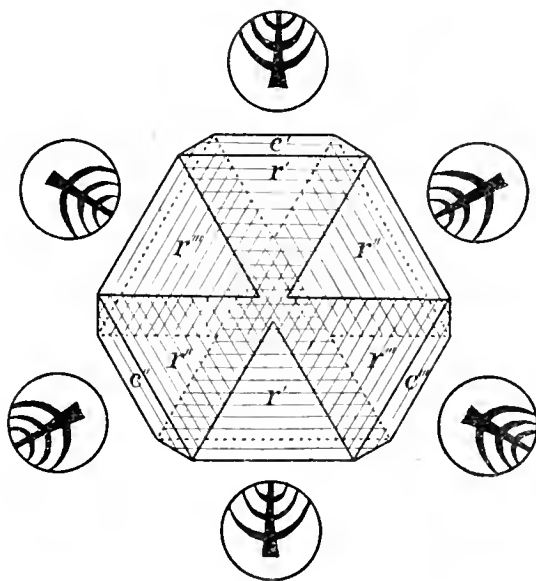


FIG. 9.

than the rest, will intercept much of the material which would otherwise go towards increasing the remaining faces. The three arms which are terminated by the faces $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$ grow outwards until the excess of supersaturation is removed, and then the crystal adjusts itself to the condition of normal equilibrium between a crystal and its solution, so that finally the gaps are filled up and a regular crystal is formed.

Triphenylmethane and Thiophen.

The determinations were exactly the same as for benzene, and the results are given in the following table and figure :

Solubility of Triphenylmethane in Thiophen.

Gram of triphenyl-methane.	Gram of thiophen.	Percent-age of triphenyl-methane.	Molecular percent-age of triphenyl-methane.	Saturation tem-perature.	Form of crystals.	Limit of metastable region.	Form of crystals.
0.5223	0.0205	96.2	89.9	87.2°	N	—	—
0.4410	0.0472	90.3	76.3	79.0	N	—	—
0.7203	0.1038	87.4	70.5	74.2	N	53.1°, 52.6°	N
0.5260	0.1145	82.1	61.3	67.2	N	49.4, 49.4	RN
0.4553	0.1008	81.9	60.8	67.0	N	50.0, 49.6	RN
0.3725	0.1008	78.7	56.0	62.7	N	51.0, 51.0	RN
0.3827	0.1288	74.8	50.6	57.6	R	51.5, 51.2	R
0.4014	0.1701	70.2	44.7	57.4	R	51.6, 51.3	R
0.6469	0.4539	58.7	32.9	53.5	R	47.5, 47.5	R
0.4771	0.5087	48.4	24.4	47.6	R	40.7, 40.3	R
0.1148	0.1482	43.6	21.1	44.0	R	—	—
0.3353	0.7411	31.1	13.5	33.5	R	25.5, 25.4	R
0.2733	0.7768	26.0	10.8	25.7	R	—	—

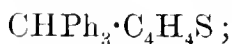
N denotes monoclinic needles (CHPh_3).

R „ rhombs ($\text{CHPh}_3 \cdot \text{C}_4\text{H}_4\text{S}$).

The curves in this case are of much the same form as with benzene, except that the solubility curve for the pure substance cuts the curve for the compound much nearer to the melting point, the thiophen compound thus having a smaller range of existence than that with benzene. The range of the “metastable region” is almost the same as in the case of benzene solutions.

The Compound of Triphenylmethane and Thiophen.

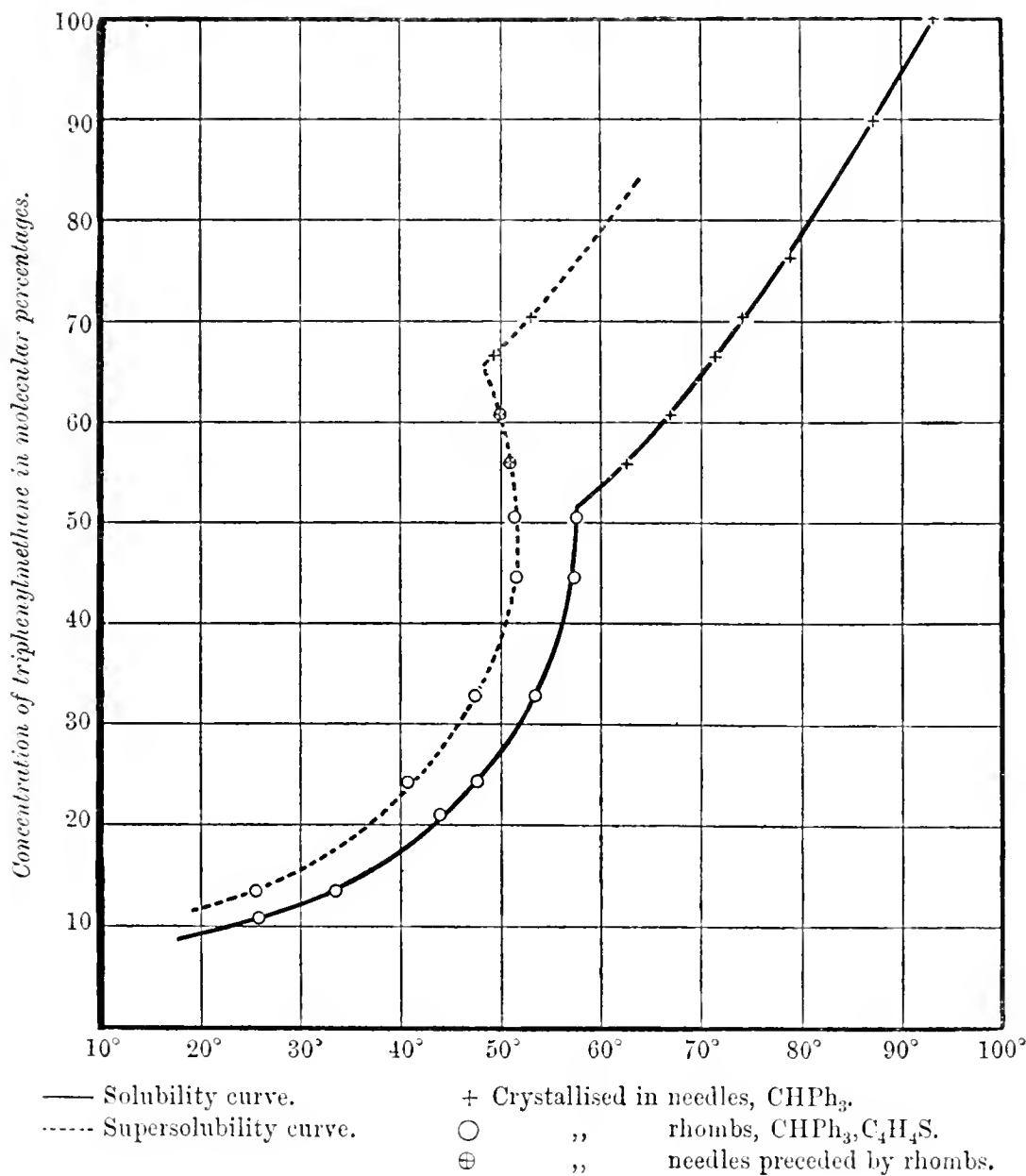
Liebermann's analysis showed that it had the composition



in crystalline form, it is exactly analogous to the benzene compound, its crystals appearing under the microscope of exactly the same form and habit, with the same twin law and similar optical properties, so that so far as microscopic evidence is of value they seem to be isomorphous. The crystals decomposed too rapidly to admit of goniometric measurement. The formation of hexagonal-shaped triplets in

which no re-entrant angles are visible shows that, as is the case with benzene, the angle between the rhombohedral edges must be approximately 60° , and the rhombohedron angle $109^\circ 28'$.

FIG. 10.—*Solubility and supersolubility curves of triphenylmethane in thiophen.*



Triphenylmethane and Pyrrole.

The results of the solubility and supersolubility determinations are given in the following table and figure :

Solubility of Triphenylmethane in Pyrrole.

Gram of triphenylmethane.	Gram of pyrrole.	Percent-age of triphenylmethane.	Molecular percent-age of triphenylmethane.	Saturation temperature.	Form of crystals.	Limit of metastable region.	Form of crystals.
0.6765	0.0166	97.6	91.8	89.2°	N	69.7°, 66.2°	N
0.7583	0.0337	95.7	86.1	86.2	N	64.6, 64.1	N
0.7528	0.0698	91.5	74.8	80.1	N	59.0, 56.9	N
0.4802	0.0887	84.4	59.8	71.1	N	51.2, 50.2	N
0.5041	0.1116	81.9	55.6	68.5	N	47.5, 42.5	N
0.7695	0.2040	79.0	50.9	65.6	N	41.5, 40.2	N
0.5570	0.1696	76.7	47.4	63.9	N	38.0, 36.5	N
0.6087	0.2279	72.8	42.3	60.8	N	35.6, 35.4	N
0.4158	0.1592	72.3	41.8	60.0	N	36.1, 35.4	N
0.6013	0.3391	63.9	32.8	53.2	N	35.3, 31.2	RN
0.4487	0.3520	56.0	25.9	46.9	N	34.4, 34.3	RN
0.3318	0.3442	49.1	20.9	42.7	N	29.8, 29.7	RN
0.3552	0.5192	40.6	15.8	36.8	N	—	—
0.2021	0.4025	33.4	12.1	31.5	R	—	—
0.2367	0.5585	29.8	10.4	29.0	R	—	—
0.2272	0.7062	24.3	8.1	24.6	R	—	—

N denotes monoclinic needles (CHPh_3).

R „ rhombs ($\text{CHPh}_3 \cdot \text{C}_4\text{H}_4\text{NH}$).

In this case the range of existence of the compound is still further restricted, its solubility curve being cut by that for the pure substance at about 33°. The break in the curve is very slight, but a determination at 31° showed that rhombs were on the more stable form at that temperature, since needles of the pure substance dissolved while the rhombs grew, whilst at 36° the converse took place, showing that the needle-shaped crystals of the pure substance were the more stable form.

In this case, the different extent of the "metastable region" for the two kinds of crystals is very well marked, for so soon as the limit for the more readily-formed rhombohedra is reached the curve falls almost vertically for a distance corresponding to 15°. In the crystallisations along this part of the curve, rhombohedra appear first in every case, and these serve as nuclei for the regular growth of crystals of pure triphenylmethane.

The Compound of Triphenylmethane and Pyrrole.

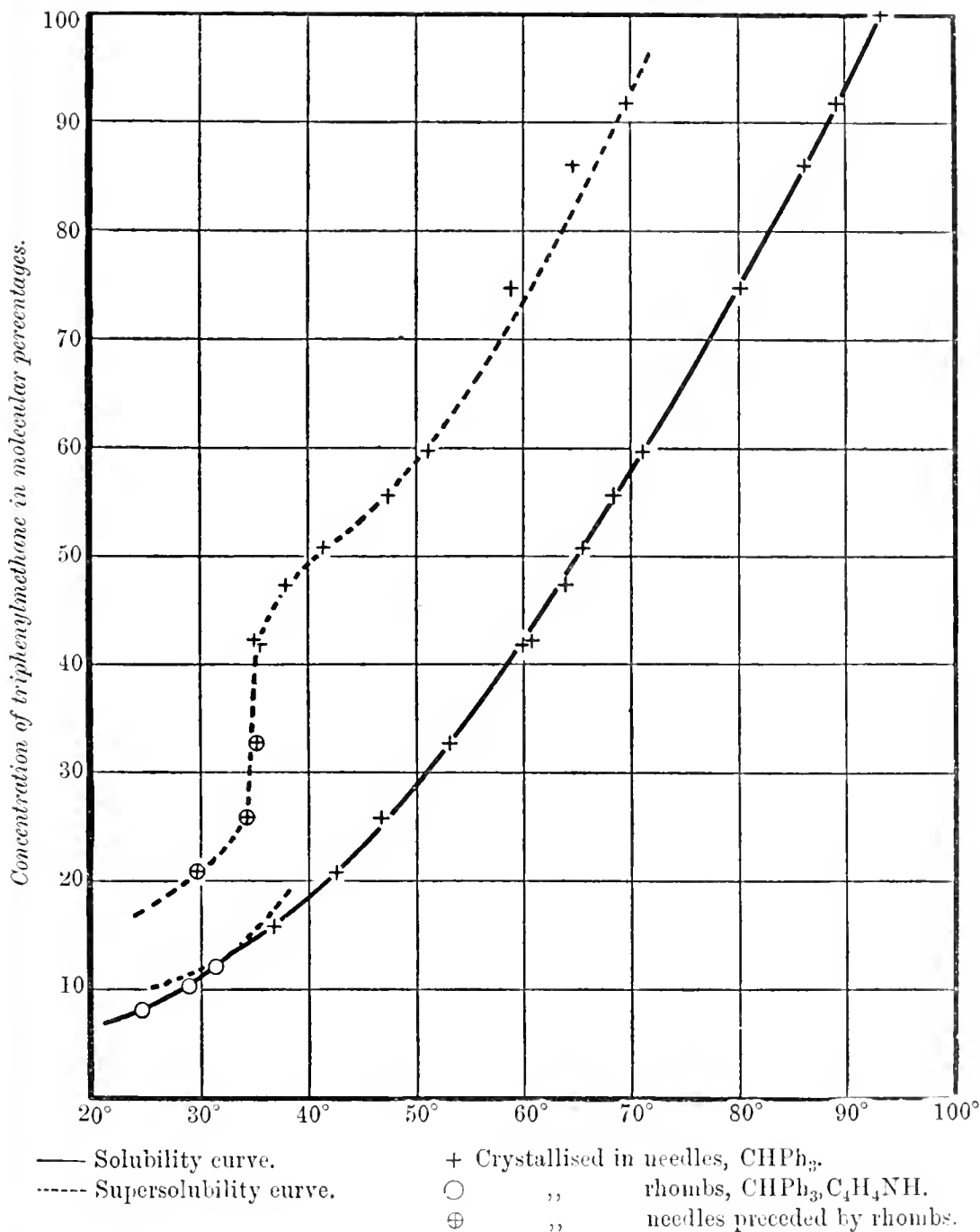
This substance had not been noticed previously, so two determinations of its composition were made by heating a known weight to 100°, with the following results:

0.1861 gram of the crystals lost 0.0388 gram on heating, corresponding to 20.86 per cent. pyrrole.

0.1762 gram of the crystals lost 0.0349 gram on heating, corresponding to 19 per cent. pyrrole.

$\text{CHPh}_3 \cdot \text{C}_4\text{H}_4\text{NH}$ requires a loss of 21.29 per cent.

FIG. 11.—*Solubility and supersolubility curves of triphenylmethane in pyrrole.*



Hence the composition is similar to that of the benzene and thiophen compounds. The crystals lose pyrrole rapidly in the air, so that the low results are easily understood. The crystals show all the same properties as those of the two former compounds, and seem to

be isomorphous with them. The tendency towards twinning is even greater in this case, and twinned crystals usually predominate over the simple rhomb. The fact that the rhombs can start the deposition of orthorhombic needles of triphenylmethane which grow on them, so that the vertical axes of both crystals are parallel, was first noticed with the pyrrole compound, as owing to the small region of stability of the rhombs it occurs much more often than with the other compounds.

Triphenylmethane and Aniline.

Solubility of Triphenylmethane in Aniline.

Gram of triphenylmethane.	Gram of aniline.	Percent-age of triphenylmethane.	Molecular percent-age of triphenylmethane.	Saturation temperature.	Form of crystals.	Limit of metastable region.	Form of crystals.
0.5157	0.0211	96.1	90.2	87.3°	N	69.1°, 68.7°	N
0.5024	0.0452	91.7	80.9	82.1	N	65.6, 64.2	N
0.5285	0.0942	84.9	68.2	74.3	N	61.1, 59.3	RN
0.4886	0.1067	82.1	63.5	71.6	N	60.7, 60.4	RN
0.4869	0.1348	78.3	57.9	70.6	R	62.4, 62.2	R
0.3750	0.1166	76.3	55.1	71.2	R	62.6, 62.4	R
0.3664	0.1416	71.7	49.1	71.6	R	62.4, 62.2	R
0.3327	0.1572	67.9	44.6	71.3	R	63.6, 63.1	R
0.2473	0.1358	64.6	40.9	70.1	R	62.4, 61.2	R
0.6066	0.5011	54.8	31.6	68.7	R	61.4, 61.1	R
0.2020	0.2258	47.2	25.4	66.0	R	59.8, 59.0	R
0.2100	0.3651	36.5	17.8	61.4	R	55.2, 53.7	R
0.1590	0.5665	21.9	9.7	52.1	R	45.2, 44.9	R
0.1465	0.9404	13.5	5.6	43.0	R	35.5, 35.0	R
0.0451	0.4312	9.5	3.8	35.3	R	—	—
0.0463	0.8061	5.4	1.85	23.0	R	—	—

N denotes monoclinic needles (CHPh_3).

R .. rhombs ($\text{CHPh}_3 \cdot \text{C}_6\text{H}_5\text{NH}_2$).

The solubility and supersolubility curves are very similar to those for benzene; the shape of the former curve indicates that the crystalline compound with the solvent, as in the case of benzene, is almost entirely dissociated in the solution.

The Compound of Triphenylmethane and Aniline.

The composition of this body was determined by weighing out a small quantity into a small flask with a rubber cork, through which passed a small tap funnel, a tube from a carbon dioxide apparatus, and another tube leading to a nitrometer filled with strong potash. Some dilute sulphuric acid was placed in the flask, and then all the air was driven out by a current of carbon dioxide; a small excess of potassium nitrite solution was then added through the tap funnel and the temperature of the flask raised slowly to 100° , when the liquid in it was boiled for ten minutes. All the evolved gases were then driven

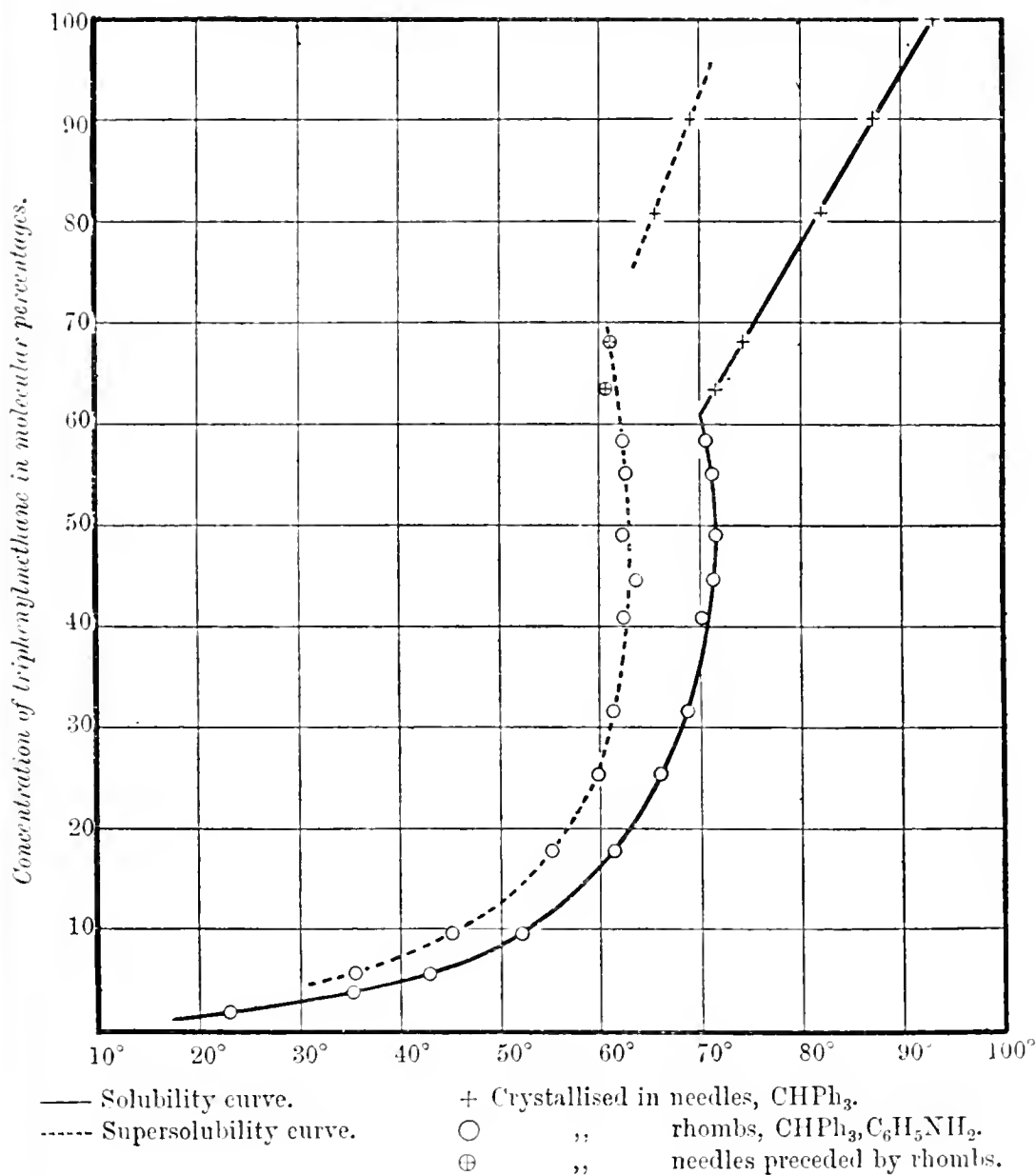
into the nitrometer by means of a current of carbon dioxide. Any traces of nitric oxide were oxidised by adding a little oxygen, the excess being absorbed with pyrogallate.

0.5856 gave 43.6 c.c. nitrogen at 19° and 759.3 mm. $N = 4.38$.

0.6926 „ 47.7 c.c. „ 20° and 756 mm. $N = 4.06$.

$\text{CHPh}_3 \cdot \text{C}_6\text{H}_5\text{NH}_2$ requires $N = 4.19$ per cent.

FIG. 12.—*Solubility and supersolubility curves of triphenylmethane in aniline.*



The substance is thus composed of molecular proportions of the two constituents as in the three previous cases; in crystalline form and habit, in twin formation, the property of causing the regular growth of orthorhombic crystals of triphenylmethane, and in optical properties,

it is practically identical with them. No evidence was found for the existence of the two modifications described by Lehmann, and it is quite clear from Lehmann's drawings that these two supposed forms are, as Hintze suggested, different habits of the same crystals.

Triphenylmethane and Pyridine.

Solubility of Triphenylmethane in Pyridine.

Gram of triphenyl-methane.	Gram of pyridine.	Percent-age of triphenyl-methane.	Molecular percent-age of triphenyl-methane.	Saturation tem-perature.	Form of crystals.	Limit of metastable region.	Form of crystals.
0.6799	0.0300	95.8	88.1	86.8°	N	—	—
0.5907	0.0550	91.5	77.2	80.6	N	—	—
0.5480	0.0915	85.7	66.4	72.8	N	—	—
0.4610	0.1017	81.9	59.7	67.8	N	46.5°, 44.7°	N
0.5132	0.1656	75.6	50.3	59.3	N	38.1, 37.7	N
0.5014	0.2138	70.1	43.5	53.1	N	28.9, 28.9	N
0.4457	0.2237	66.6	39.5	48.7	N	24.1, 24.0	N
0.3800	0.2800	57.6	30.7	37.9	N	—	—
0.3332	0.2918	53.3	27.2	31.7	N	—	—
0.2139	0.2486	46.2	22.0	22.8	N	—	—

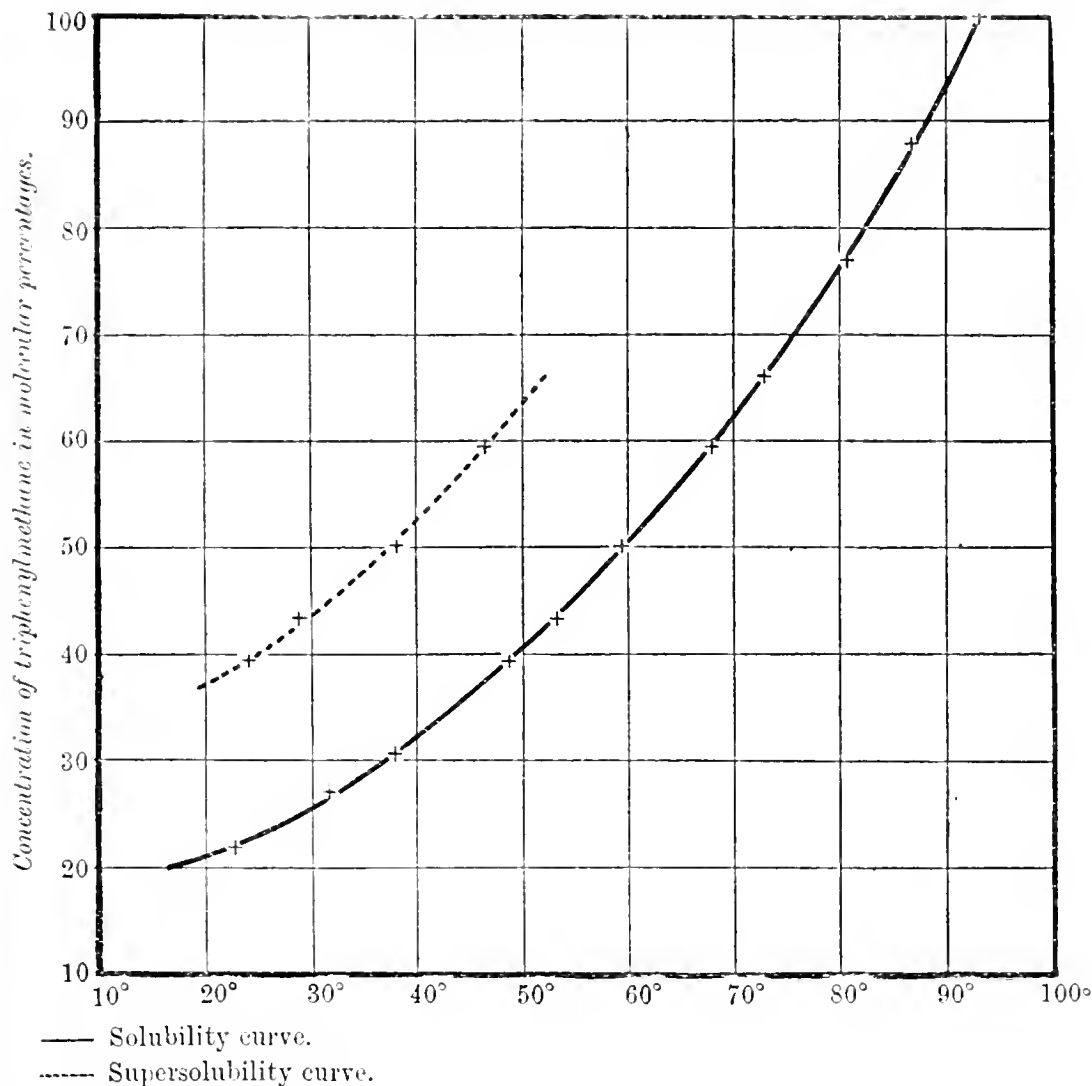
In this case no compound is formed, and the solubility curve shows no break. Only a few determinations of the limit of the "metastable region" could be made, as at temperatures above 70° the contents of the tubes became yellow owing to the presence of some decomposition product which seemed to disturb the normal course of crystallisation, for on cooling crystals did not, as in the other tubes, appear in the body of the liquid, but at some point on the glass.

The Spontaneous Crystallisation of Supersaturated Solutions.

Ostwald's classification of supersaturated solutions as "metastable" and "labile," according as they have or have not the property of spontaneous crystallisation, has been criticised by de Coppet (*Bull. Soc. chim.*, 1901, 25, 388), who contends that there is no real distinction between the two classes. Arguing from a molecular theory of solution, de Coppet points out that crystallisation is produced by some particular concurrence of the solute molecules, which must happen sooner or later in any supersaturated solution, however small may be the degree of supersaturation. The probability that crystallisation will take place within a given time is obviously greater in a more concentrated solution, and de Coppet attributes the apparent difference between metastable and labile solutions to the different time required for crystallisation in the two cases. He has studied (*Bull. Soc. chim.*, 1872, 17, 146, and *loc. cit.*) the crystallisation of sodium sulphate by allowing sealed tubes containing a solution to cool until they were

supersaturated and deposited crystals, but his experiments were not made over a sufficient range of concentration or under sufficiently definite conditions to give him a decisive result. They distinctly indicate, however, the existence of a "metastable limit," as crystals of $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ never appeared in the solution until 12° below the saturation temperature. De Coppet does not admit that his results bear this interpretation, as in many instances tubes with the same

FIG. 13.-- *Solubility and supersolubility curves of triphenylmethane in pyridine.*



concentration crystallised at different temperatures, and the same tube in successive experiments gave very different results. This is not surprising, since de Coppet allowed his tubes to cool without shaking, and in a solution that is left undisturbed crystallisation may be deferred to an irregular, and at present unexplained, extent; vigorous shaking seems to be the surest way to make a solution crystallise as soon as it is capable of doing so.

The experiments of Miers and Miss Isaacs (Trans., 1906, 89, 413) and those described in the present paper definitely prove the existence of a "metastable limit" in the case of solutions both in water and organic liquids. It is represented by the supersolubility curve, which gives the temperature at which solutions of different concentration crystallise spontaneously when cooled with constant shaking, that is, the temperature at which they pass from the metastable to the labile condition. This curve is always found to run approximately parallel to the solubility curve, at a distance from it depending on the respective solute and solvent. No instance was found in the large number of experiments made to determine these curves in which a solution freed from crystalline nuclei by previous heating crystallised when in the metastable region: so that it would seem that the difference between the two kinds of solutions is something more than one of degree.

Ostwald is inclined to be sceptical of kinetic theories of solution and crystallisation, and looks to the phenomena of surface energy for an explanation of these questions. The kinetic theory of crystallisation has, however, so many advantages as a guide in experimental work that it is as well to see if it cannot throw some light on the facts observed. Ostwald's criticism of it is based mainly on some observations of de Boisbaudran and of Gernez on the "inertia" of crystal faces towards small changes of concentration, and on some observations respecting the effect of crystals on supersaturated solutions of salts isomorphous with them. It must be noticed that all these were merely qualitative observations which have not received quantitative proof. In the solubility method used by the authors in the present paper, no trace of this inertia was perceptible; on the other hand, very small changes of temperature produced immediate effects on the appearance of the faces of the crystal when the solutions were well stirred, a condition which is not mentioned by either of the above authors.

If we consider crystallisation and solution from the kinetic standpoint, we must suppose that a solvent has the power to carry off molecules from the surface of a crystal by some chemico-physical action, the exact nature of which is not yet known. This action is opposed by the attractive force exerted by the molecules in the crystal on one another, and on any solute molecules which approach the crystal from the solution: so that it is the combined effect of these two forces producing erosion and accretion which conditions crystalline growth. The attractive force acting on a particular molecule must be due to a limited number of molecules in its immediate neighbourhood. When crystals are large compared with molecular distances, this force will assume its maximum value at all points

on a crystal face except near the edges, where, as Willard Gibbs has pointed out, the force protecting the molecules of the crystal from erosion will be smaller than at the centre. As the size of a crystal is diminished, the variation of this molecular force will gradually become more perceptible, as every point on a crystal face comes nearer and nearer to an edge. Decrease in size will therefore be accompanied by an increase in solubility. This question has been studied by J. J. Thomson and others from a consideration of the surface energy of a crystal; their conclusions as to the relation of solubility to size have been verified by Ostwald (*Zeit. physikal. Chem.*, 1900, **34**, 495) and by Hulett (*Zeit. physikal. Chem.*, 1901, **37**, 385).

Why then should a supersaturated solution exist without crystallising? On the kinetic theory of solution, molecules of the solute must constantly collide with and exert attractive forces on one another, so that there seems to be no reason why some small number of molecules should not meet and form a nucleus for crystallisation by the gradual accretion of other molecules. The explanation why this does not lead to crystallisation in the metastable region probably lies in the variation of molecular forces in the early stages through which a crystal formed in this way has to pass. A solution which is but slightly supersaturated for microscopic crystals would be unsaturated for the very small crystal individuals which must be the first products in a spontaneous crystallisation. It is therefore probable that these would be dispersed before they could pass through the critical stages of their early growth; for it must be remembered that in these stages not only is the erosive action of the solvent more powerful, but also the attractive force of the crystals on solute molecules is relatively smaller; thus the time necessary for growth and the probability that the crystal will be dispersed are both increased. Up to a certain limit of supersaturation it would not be surprising if it were impossible for a crystal to persist through these initial stages, but when the supersaturation became large enough to counteract the increased solubility of the incipient crystal, spontaneous crystallisation would take place within a longer or shorter period, depending on certain physical conditions. Supposing these to be favourable, as seems to be the case when the solution is vigorously shaken or stirred, we might expect crystallisation to start at a number of different points in the liquid and to proceed rapidly, exactly as was observed in the experiments previously described. During the initial stages of growth, the solution, although it is giving up dissolved matter to the crystals, is also quickly becoming more supersaturated with respect to them, hence, at the start, the rate of growth should be very rapid; this agrees with the observations of Richards and Archibald (*Proc. Amer.*

Acad., 1901, **36**, 341), who photographed the various stages of development of a crystal.

It is thus possible to explain from a kinetic standpoint why supersaturation is so general a phenomenon and why there should be a metastable limit dividing solutions which will crystallise spontaneously from those which will not.

The production of crystals in a metastable solution differs from the formation of liquid drops in a metastable supersaturated vapour, as in the latter case any foreign body, for example, a dust particle, or the walls of the containing vessel, is able to produce condensation, while in the former only a body with an identical or closely related crystal structure can start crystallisation. In some of the experiments made to determine the supersolubility described in the present paper, particles of foreign matter were visible in the tubes, but these did not bring about crystallisation, which occurred regularly throughout the liquid and did not start from the solid impurities present.

Thus, in a metastable solution, the presence of a surface exerting definitely orientated molecular forces is necessary to give rise to a definite crystal structure.

Since writing the above, the authors have found that a somewhat similar explanation of the nature of metastable and labile solutions has already been given by Küster (*Zeit. anorg. Chem.*, 1903, **33**, 363).

Summary.

(1) Kuriloff's method for determining solubilities has been slightly modified, and has been found very useful when only small quantities of substance are available and the solvent is volatile. It also admits very easily of the determination of the limit of the "metastable region" of a solution, that is, the temperature at which crystals are spontaneously produced without the addition of crystalline nuclei.

(2) The solubility of triphenylmethane in benzene, thiophen, pyrrole, aniline, and pyridine has been determined; the results for benzene agree with those of Kuriloff.

(3) Triphenylmethane crystallises in certain circumstances from solutions in benzene, thiophen, pyrrole, and aniline with one molecule of the solvent combined in a manner similar to that of "water of crystallisation."

(4) Micro-copic examination of the four compounds has shown that they have almost identical crystalline forms with the same habit, twin law, and optical properties, so that they probably form an isomorphous series.

(5) Rhombohedral crystals of each of these compounds have the property of causing the growth of orthorhombic crystals of triphenyl-

methane when placed in solutions which are metastable as regards the latter body. This is additional evidence in favour of their isomorphism.

(6) The "supersolubility curve," that is, the limit of the "metastable region," has been determined in each case. For all five solvents the curve runs approximately parallel to the solubility curve, being about 20° distant from it for the crystallisation of pure triphenylmethane, and about 7° distant for the crystallisation of the compounds containing a molecule of solvent.

The authors wish to express their indebtedness to Mr. B. M. Jones, late Scholar of Balliol College, for his valuable assistance in a number of the determinations, and to Mr. D. H. Nagel, Trinity College, Oxford, for the interest he has taken in the progress of their work.

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CVI.—*Studies of Dynamic Isomerism. Part IV.* *Stereoisomeric Halogen Derivatives of Camphor.*

By THOMAS MARTIN LOWRY.

It has been shown (Lowry, *Trans.*, 1898, **73**, 569) that on brominating α -chlorocamphor and on chlorinating α -bromocamphor mixtures are formed of the isomorphous stereoisomerides represented by the formula

$C_8H_{14} \begin{smallmatrix} \text{CClBr} \\ \diagdown \\ \text{C} \\ | \\ \text{CO} \end{smallmatrix}$, the isomerism depending on the asymmetry of the

α -carbon atom. Similar isomerides are also obtained by the action of halogens on nitrocamphor (*Trans.*, 1898, **73**, 986—991), but as these are not isomorphous, it is possible by repeated crystallisation to isolate each compound in a pure state.

Whilst the α -derivatives thus appear invariably to yield a mixture of isomerides (compare Forster, *Trans.*, 1902, **81**, 160), it is possible to obtain from camphor itself an almost theoretical amount of a single bromo-derivative, the well-known α -bromocamphor. Even in this case, however, it has long been supposed that two isomerides are formed initially, one of which undergoes isomeric change during the subsequent purification. Thus, Marsh, in 1891 (*Trans.*, **59**, 968), was able to separate from the initial product a fraction which differed widely from α -bromocamphor, its optical rotatory power being $[\alpha]_D + 29.4^\circ$ only, whilst that of the ordinary bromocamphor is $[\alpha]_D + 135^\circ$. Marsh found

that by distilling under atmospheric pressure the low-rotatory compound was largely converted into ordinary bromocamphor, and proposed to use this method in order to purify the crude product.

A far more effective method of purification had, however, been introduced by Armstrong in 1878 (*Chem. News*, **37**, 4). This consisted in the use of alcoholic potash, and there could be no doubt that this agent served not only to remove hydrogen bromide and to reduce any dibromocamphor that might be present, but also to convert into the stable α -compound any isomeric bromocamphor which might be formed by the action of the halogen.

On account of the large proportion of α -bromocamphor obtained by Armstrong's method, it has been generally supposed that the conversion of the labile into the stable isomeride was complete and non-reversible. Kipping has, however, recently shown (*Proc.*, 1905, **21**, 125) that there is in the alcoholic solution a marked reversal of the isomeric change. By working alternately in alkaline and in acid solution he was able to prepare from pure α -bromocamphor a product of low rotatory power, very similar to that described by Marsh. When alkali was added to a concentrated alcoholic solution of this substance, crystals of α -bromocamphor separated; in less concentrated solutions, the product remained dissolved and was found to have the same rotatory power, $[\alpha]_D + 122^\circ$, as that prepared directly by the action of alkali on α -bromocamphor.

The principle of the method by which solubility measurements may be applied to determine the equilibrium between dynamic isomerides has been described in two previous papers (*Trans.*, 1904, **85**, 1541, 1551). In the case of the stereoisomeric bromocamphors, the application of the method is rendered exceptionally easy by the fact that isomeric change takes place only in presence of added alkali, and is therefore completely under control. The difficulty previously encountered in determining the initial solubility of the unchanged material is therefore absent, and after adding the alkali the final equilibrium is very quickly attained. The facility of the method proved to be such that the observations were extended, not only to chlorocamphor (the isomeric change of which had already been noted by Kipping), but also to several of the dihalogen derivatives of camphor; the further application of the method to the sulphonic derivatives of camphor is described in a subsequent paper.

It should be noted that whilst it is possible to determine by means of solubility measurements the approximate proportions in which the isomerides are in equilibrium in solution, and to estimate roughly the rotatory power of the α' -compounds, physical methods of this kind can form no adequate substitute for the actual separation of these substances which has been undertaken by Kipping. The chief advantage of the physical methods is that they enable a rapid survey to be

made of the behaviour of a range of compounds far exceeding the number which could well be submitted to the tedious process of fractionation.

1. The substances investigated were :

α - and β -bromocamphor and α -chlorocamphor.

$\alpha\beta$ - and $\alpha\pi$ -dibromocamphor.

$\alpha\beta$ - and $\alpha\pi$ -chlorobromocamphor.

$\alpha\alpha'$ -Dibromocamphor could not be used, as its alcoholic solutions soon decomposed, becoming yellow on exposure to the air. Measurements were made, however, of a trisubstituted compound, a $\pi\alpha\alpha'$ -chlorobromo-

nitrocamphor, $C_8H_{10}Cl \begin{smallmatrix} CBrNO_2 \\ | \\ CO \end{smallmatrix}$, obtained by the action of nitric

acid on crude $\pi\alpha$ -chlorobromocamphor. The solvent used in the majority of cases was absolute alcohol of 99.5 per cent. concentration, but observations were also made of the solubility of α -bromocamphor and α -chlorocamphor in ethyl alcohol of lower concentration and in commercial methyl alcohol. The alkali was made by dissolving sodium in the alcohol, and was added in such proportions as to give solutions of approximately known strength, usually $N/100$, $N/500$, or $N/1000$.

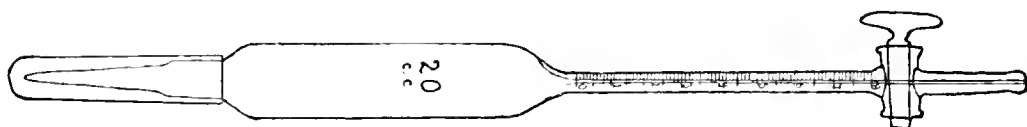
2. The saturated solutions were prepared by stirring the solid with the solvent in a large test-tube supported in a water-bath. The bath was stirred mechanically and was kept at a constant temperature by means of an automatic gas-regulator. The majority of the measurements were made within one- or two-hundredths of 20° as determined by a thermometer graduated to 0.01° , which had recently been standardised at the Reichsanstalt.* As no isomeric change took place until alkali was added, it was not necessary to secure saturation rapidly. The solid was therefore added in coarse crystals and, after stirring during one or two hours, was allowed to settle. Samples of the saturated solution were then withdrawn by means of a warm pipette and could be used immediately; as filtration was unnecessary, the chief risk of change in concentration taking place was thus avoided.

3. The solubilities were determined by evaporating weighed quantities of the saturated solutions in weighing bottles. In the case of the monohalogen compounds, considerable care was needed to avoid loss by sublimation; the solutions were gently heated on the top of an air-oven and the temperature was adjusted, so that from twelve to thirty-six hours were required for the evaporation of 10 c.c. of the alcoholic solution. In the case of the dihalogen compounds, no such trouble was experienced, but some of the sulphonic compounds referred to in the

* By using one of the spiral regulators recently described (Trans., 1905, 87, 1030), the temperature of one of the baths was maintained without readjustment between 20.00° and 20.02° whenever the bath was in use throughout the six months from September, 1905, to March, 1906.

following paper formed compact crystals, and it was necessary to heat these more strongly in order to expel the last traces of the solvent.

4. The densities were determined by means of a special form of graduated pipette (Fig. 1), the ordinary Meyerhoffer-Saunders pipette not being suited to the conditions of experiment. The pipette was heated to 20° in the thermostat and quickly lowered into the tube containing the saturated solution. The solution was drawn up into the narrow graduated stem, the tap closed, and the position of the meniscus noted. The capillary point was then wiped and covered with a glass cap to prevent evaporation during the weighing. The earlier experiments were made with a pipette of 42 c.c. capacity, provided with a thermometer: this had been designed and calibrated by Mr. W. R. Bousfield, to whom I am indebted for the loan of the instrument.



Graduated pipette for determining the density of saturated solutions.

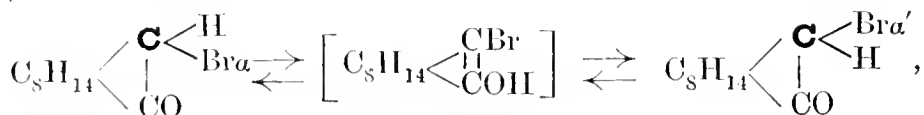
FIG. 1.

Duplicate determinations (compare β -bromocamphor) usually differed by only a few units in the fourth place of decimals; the densities shown in brackets were not measured, but were calculated with sufficient exactness by assuming that each 1 per cent. of solute increased the density of the alcohol by 0.004. The experiments described in the subsequent paper were made with pipettes of the pattern figured and had capacities of 10 and 20 c.c. only.

5. The rotatory powers of the solutions were determined by means of a polarimeter graduated to read to 0.001° by means of a vernier. This instrument, which was made to the design of the late Mr. J. W. Rodger, is provided with exceptionally large optical parts, the triple field being divided horizontally. For the loan of this I am indebted to the Board of Education, and desire to express my indebtedness to Prof. Tilden, through whom permission was obtained to use the instrument. The polariser and analyser are mounted on separate bases, an important point when jacketed tubes are used, and are supported on a teak base provided with V-grooves. The temperature of the 2-dm. tubes is maintained at 20° by enclosing them in a hollow copper jacket through which water is circulated from a large thermostat. The circulation is maintained by an eccentric pump driven by an electromotor, the speed of which can be varied by lamp resistances.

Solnte.	Solvent.	Alkali.	Density of saturated solutions.		Concentration of saturated solutions.					Rotatory power of saturated solutions.									
			α .	$\alpha \rightleftharpoons \alpha'$.	Grams per 100 grams of solvent.		Ratio.	α .	$\alpha \rightleftharpoons \alpha'$.		Ratio.	α .	$\alpha \rightleftharpoons \alpha'$.		α .	$\alpha \rightleftharpoons \alpha'$.		$[\alpha]_D$.	
					α .	$\alpha \rightleftharpoons \alpha'$.			α .	$\alpha \rightleftharpoons \alpha'$.			α .	$\alpha \rightleftharpoons \alpha'$.		α .	$\alpha \rightleftharpoons \alpha'$.		
Per cent.																			
α -Bromocamphor	EtOH	N/1000	0.8536	0.8618	21.1	23.7	0.89	14.9	16.5	0.90	41.0	41.6	+138	+126	< +18				
"	EtOH	N/100	0.854	0.863	20.5	23.3	0.88	14.5	16.3	0.89	40.5	40.8	+139	+125	< +9				
"	EtOH	N/1000	—	—	20.2	23.1	0.87	—	—	—	—	—	—	—	—	—	—	—	
"	EtOH	N/1000	0.855	0.862	18.8	21.5	0.88	—	—	—	—	—	—	—	—	—	—	—	
"	MeOH (concl.)	N/100	0.860	0.868	23.2	25.9	0.89	16.2	17.8	0.91	42.7	43.1	+132	+121	< +12				
β -Bromocamphor	EtOH	N/1000	0.8506	0.8503	19.5	19.3	1.01	13.8	—	—	5.30	5.32	+19	—	—	—	—	—	
α -Chlorocamphor	EtOH	N/100	0.825	0.830	15.9	18.2	0.87	11.3	12.8	0.885	22.65	23.6	+100	+92	< +34				
"	MeOH (concl.)	N/100	0.830	0.835	17.5	20.1	0.87	12.3	13.9	0.884	23.9	24.75	+97	+89	< +27				
β -Dibromocamphor	EtOH	N/1000	0.805	0.807	3.18	3.58	0.89	2.48	2.79	0.89	4.92	4.54	+99	+81	-61				
"	EtOH	N/1000	—	—	3.26	3.64	0.90	2.54	2.83	0.90	4.93	4.59	+97	+81	-58				
β -Chlorobromocamphor.	EtOH	N/500	0.805	0.807	4.00	4.42	0.90	3.22	3.57	0.90	4.22	3.98	+65	+55	-34				
π -Dibromocamphor	EtOH	N/1000	[0.799]	[0.800]	2.09	2.35	0.89	1.64	1.83	0.89	3.22	3.62	+98	+99	+105				
π -Chlorobromocamphor.	EtOH	N/1000	[0.804]	[0.806]	3.20	3.65	0.88	2.49	2.84	0.88	4.24	5.10	+85	+90	+123				
$\alpha\alpha'$ -Chlorobromonitro- camphor	EtOH	N/1000	0.801	0.801	2.61	2.61	1.00	2.04	2.04	1.00	5.00	5.01	+121	—	—	—	—	—	

The table shows the numerical values obtained. It will be noticed that in the case of all compounds containing the group $-\text{CHBr}\cdot\text{CO}-$ or $-\text{CHCl}\cdot\text{CO}-$ the addition of a mere trace of alkali is followed by a marked increase in the density and concentration of the saturated solutions, the ratio of the initial to the final solubility remaining almost constant at 0.88 to 0.90 throughout the series. No change of solubility occurred in the case of β -bromocamphor, $\text{C}_8\text{H}_{13}\text{Br}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CO} \end{smallmatrix}$, in which both α -positions are occupied by hydrogen, nor in the case of $\pi\alpha\alpha'$ -chlorobromonitrocarnphor, $\text{C}_8\text{H}_{13}\text{Cl}\begin{smallmatrix} \text{CBr}\cdot\text{NO}_2 \\ | \\ \text{CO} \end{smallmatrix}$, in which both these hydrogen atoms have been displaced. It is thus evident that, although isomeric change probably takes place through an intermediate enolic form,



the increase of solubility must be attributed mainly to the interchange of the radicles occupying the α and α' positions. The case is somewhat analogous to that of glucose, mannose, and fructose studied by Lobry de Bruyn (*Rec. trav. chim.*, 1895, 14, 201); in each case the isomerides have a common enolic form, but the proportion of this in the neutral solutions is so small that no isomeric change takes place until alkali is added.

Proportions in which the Isomerides are in Equilibrium in Solution.—In order to deduce from the solubility measurements the proportions of the isomerides in the alkaline solutions, it was necessary to ascertain whether the α' -form would be likely to influence the solubility of the α -isomeride. Direct experiments were not practicable, but the following observations were made to test this point.

1. The solubility of $\alpha\beta$ -dibromocamphor was determined (*a*) in alcohol, (*b*) in alcohol containing 0.50 gram of $\alpha\pi$ -dibromocamphor per 100 grams of alcohol. The total amount of solid per 100 grams of alcohol in the two saturated solutions was found to be:

(<i>a</i>) 3.24	3.27	Mean, 3.26 per cent.
(<i>b</i>) 3.76	3.75	3.76 Mean, 3.76 „
<hr/>		
Difference		0.50 per cent.

The solubility of $\alpha\beta$ -dibromocamphor is thus not affected by the addition of 0.5 per cent. of the $\alpha\pi$ -isomeride, and it is probable that the presence of 0.4 per cent. of the $\alpha'\beta$ -isomeride would have equally little effect. In the case of the sparingly soluble dihalogen compounds

the solubility measurements can therefore be directly applied to determine the proportions of the isomerides in the solutions. These are practically uniform throughout the series, the amount of the α -form being 89 per cent. of the total matter in solution, and the ratio $\alpha : \alpha' = 8 : 1$ approximately.

2. The solubility of α -bromocamphor was determined (*a*) in alcohol, (*b*) in alcohol in which 2 per cent. of the β -isomeride had been dissolved. The total amounts of dissolved solid per 100 grams of alcohol were found to be :

(<i>a</i>)	21.18	21.09	21.15	Mean, 21.14 per cent.
(<i>b</i>)	24.21	24.19	24.25	Mean, 24.22 „

Ratio = 0.873. Difference = 3.08 per cent.

The densities at 20°/4° were 0.8536 and 0.8616 and the volume concentrations 14.89 and 16.78 grams per 100 c.c.; ratio, 0.888. The actual proportion of the α -compound in the artificial mixture, 0.917, is higher than either of the above ratios, the solubility being increased by the presence of the isomeride. In the case of the mixture formed by the action of alkali on α -bromocamphor the percentage by weight increases in the ratio 0.88 : 1, the percentage by volume in the ratio 0.90 : 1; the proportion of the α -compound is therefore probably 0.93, and the ratio $\alpha : \alpha' = 13 : 1$ approximately.

No direct measurements were made with reference to the influence of an isomeride on the solubility of α -chlorocamphor, but the solubility-ratios, 0.87 by weight and 0.89 by volume, probably correspond to about 91 per cent. of the α -compound in the solution.

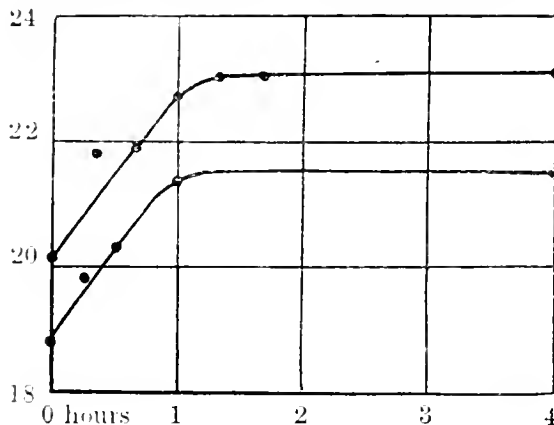
Whilst these values are probably correct within 1—2 per cent., the high solubility of α -bromocamphor and α -chlorocamphor places them beyond the limits within which it was originally proposed to apply the solubility method to determine the proportions of dynamic isomerides in solution.

Rotatory Power of the Isomerides.—On referring to the table, it will be seen that the increased concentration which follows the addition of alkali is usually accompanied by an increase in the rotatory power, α_D , of the saturated solution. In the case of $\alpha\beta$ -dibromocamphor and $\alpha\beta$ -chlorobromocamphor, the rotatory power decreases and the products of change are evidently levorotatory. In other cases the products, although dextrorotatory, must as a rule be less active than the original material, since the specific rotatory power, $[\alpha]_D$, of the $\alpha \rightleftharpoons \alpha'$ mixture is less than that of the α -compound. Exceptions are found in the case of $\alpha\pi$ -dibromocamphor and $\alpha\pi$ -chlorobromocamphor, which show a slight increase of specific rotatory power on the addition of alkali.

These exceptions afford an illustration of the fallacy underlying the

"Principle of Optical Superposition," to which attention has been directed by Rosanoff (*J. Amer. Chem. Soc.*, 1906, **28**, 525). If this principle were valid, the change of rotatory power following from a reversal of the asymmetry of the α -carbon atom should be independent of the configuration of the rest of the molecule, and could not possibly be opposite in sign in compounds so closely related as the β - and π -bromocamphors. Such irregularities can, however, be understood if it be recognised that a change in the balancing of a single carbon atom may, and indeed must, disturb the balance of the whole molecule and affect every centre of asymmetry. Until much more information is available, it will evidently not be possible to make any important generalisation as to the rotatory power of compounds containing

FIG. 2. — *Solubility of α -bromocamphor in alcohol with N/1000 sodium ethoxide.*



several centres of asymmetry, especially when these are connected together in a complex ring system as in the case of camphor and the cyclic terpenes.

Whilst the rotatory powers of the solutions give a rough idea of the optical properties of the α' -compounds, accurate values cannot be deduced on account of the small concentrations of these compounds and the presence of a large excess of the α -isomerides. In the case of the monohalogen derivatives, it must further be recognised that the increased concentration which follows the addition of alkali is not wholly due to the formation of the α' -compound, since an additional quantity of the α -compound also passes into solution. If a correction be made for this, it appears probable that α' -bromocamphor is levorotatory and α' -chlorocamphor only feebly dextro-rotatory; the uncorrected figures given in the table are maximum values only.

Velocity of Isomeric Change.

Two experiments in which alkali was added to the extent of $N/100$ showed that equilibrium was already attained in an alcoholic solution of bromocamphor at the end of 0.6 and 0.7 hour. When the quantity of alkali was reduced to $N/1000$, regular curves were obtained which showed a gradual increase of solubility during the first hour, after which the solubility remained constant. The curves shown represent two series of experiments with alcohol of 98.7 and 97 per cent. concentration, and indicate that the rate of change is not increased by doubling the proportion of water in the alcohol. When the quantity of alkali was further reduced to $N/10,000$, the change became exceedingly slow, and it is probable that the alkali becomes used up either in reducing the bromocamphor or in neutralising traces of acid formed in the solution.

$\pi\alpha\alpha'$ -Chlorobromonitrocaphor.—This compound, prepared by the action of nitric acid on the crude chlorobromocamphor produced by heating α -bromocamphor- π -sulphochloride, is, like the chlorobromocamphor itself, contaminated with a certain amount of the isomorphous dibromocamphor (0.2352 gave 0.2565 AgCl + AgBr; Cl + Br = 38.0. $C_{10}H_{13}O_3NClBr$ requires Cl + Br = 37.2 per cent.). The mixture behaved in almost every respect like a pure substance, melted sharply at 138° , showed a constant solubility in alcohol, and crystallised magnificently.

Measurable crystals were obtained from a solution in acetone which was allowed to cool slowly to the atmospheric temperature. They belonged to the orthorhombic system and gave the following constants:

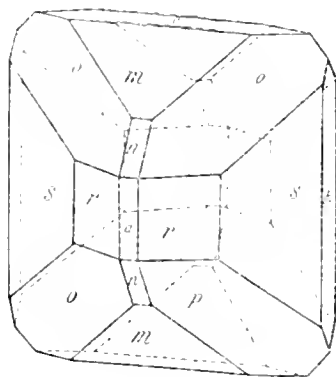


FIG. 3.

Forms present : $a\{100\}$, $b\{010\}$, $c\{001\}$, $o\{111\}$,
 $n\{101\}$, $m\{102\}$, $r\{110\}$, $s\{120\}$;

a , b , and c were only occasionally observed.

Axial ratios : $a : b : c = 0.889 : 1 : 1.049$.

Angles measured :

<i>ar</i> 100 : 110	(27)	41°39'	—	<i>nm</i> 101 : 102	(4)	19°20'	(19°11')
<i>rs</i> 110 : 120	(30)	18°57'	(19°0')	<i>ro</i> 110 : 111	(36)	32°21'	—
<i>ss</i> 120 : 120	(15)	58°48'	(58°42')	<i>co</i> 001 : 111	(20)	57°40'	(57°39')
<i>am</i> 100 : 102	(13)	59°34'	(59°28')	<i>mo</i> 102 : 111	(6)	38°40'	(38°35')
<i>em</i> 001 : 102	(11)	30°27'	(30°32')	<i>os</i> 111 : 120	(6)	36°53'	(36°59')
<i>an</i> 100 : 101	(3)	40°13'	(40°17')	<i>sm</i> 120 : 102	(6)	104°15'	(104°25')

Summary.—(1) The method previously employed in the case of nitrocamphor and the sugars to determine the proportions in which the dynamic isomerides are in equilibrium in solution has been applied to the halogen derivatives of camphor, which have been shown by Kipping to undergo reversible isomeric change in presence of alkalis.

(2) In the case of each compound containing the group $-\text{CHBr}\cdot\text{CO}-$ or $-\text{CHCl}\cdot\text{CO}-$, the addition of alkali is followed by an increase in the concentration of the saturated solution in the ratio 0.89:1 approximately.

(3) The proportion of the α' -form is probably about 7 per cent. in the case of bromocamphor, 9 per cent. in the case of chlorocamphor, and 11 per cent. in the case of the $\alpha\beta$ - and $\alpha\pi$ -dihalogen compounds.

(4) No increase of solubility is observed in the case of β -bromocamphor or of the $\alpha\alpha'$ -derivatives.

(5) Approximate values are given for the rotatory powers of the α' -compounds. α' -Bromocamphor is probably levorotatory, and α' -chlorocamphor only feebly dextrorotatory.

A part of the expense incurred in the inquiry described in this and the following paper was defrayed by grants from the Research Fund of the Chemical Society and from the British Association. The author wishes to take this opportunity of expressing his indebtedness for the help thus afforded.

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CVII.—*Studies of Dynamic Isomerism. Part V.* *Isomeric Sulphonic Derivatives of Camphor.*

By THOMAS MARTIN LOWRY and EGBERT H. MAGSON, B.Sc.

In the previous paper it has been shown that the reversible isomeric change which α -bromocamphor, α -chlorocamphor, and their β - and π -halogen derivatives undergo when a trace of alkali is added to their alcoholic solutions (Kipping, *Proc.*, 1905, 21, 125) is accompanied by a marked increase in the concentration of the saturated solutions. Similar experiments are now described in the case of some twenty com-

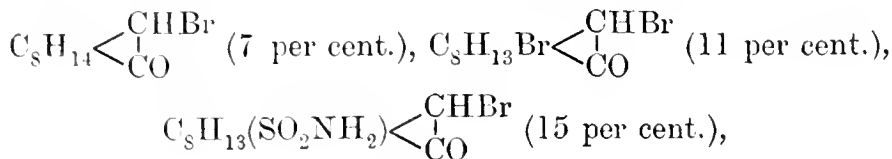
pounds containing a sulphonic group; the majority of these belong to the Reychler or β -series (Armstrong and Lowry, *Trans.*, 1902, 81, 1441), only a few measurements of the π -sulphonic compounds being included for the sake of comparison. The methods adopted were identical with those previously used; the results, which are shown in a table, represent in almost every case the mean of a number of determinations, special care being taken to ensure that the solid α -compounds were initially free from the α' -isomerides. The solubility of the metallic sulphonates was determined in aqueous solutions to which ammonia was added; in the other cases, the solvent was alcohol of 99.5 per cent. strength and the alkali *N*/500 or *N*/1000 sodium ethoxide.

I. *Derivatives of Camphor- π -sulphonic Acid.*

The behaviour of the π -sulphonic compounds is relatively simple. Kipping has shown that the salts both of α -bromo- and of α -chloro-camphor- π -sulphonic acid undergo isomeric change in presence of a trace of free alkali. No evidence has been obtained of the formation of lactonic rings between the κ and π -positions, and the isomerism appears to be of the same simple character as in the case of bromo-camphor itself. By fractionally crystallising the hydrindamine salts, Kipping has isolated the acids in which the halogen occupies the α' -position (*Proc.*, 1905, 21, 293), and has thus solved the problem presented by this series of isomeric changes. The measurements now described were therefore made, not so much in order to secure additional information with reference to this group of compounds as to test the method of experiment and to determine to what extent the changes noted amongst the β -compounds were due to simple stereo-isomerism on the one hand, or to lactone formation on the other.

The most suitable salts for solubility measurements are the ammonium salts, the relatively small solubility of which is made use of in isolating the sulphonic acids of the π -series. The solubility of ammonium α -bromocamphor- π -sulphonate in water was found to be 18.57 per cent. at 20°, but repeated determinations of the density of the saturated solution showed that no increase of solubility followed the addition of ammonia or of traces of caustic soda. This unexpected result is not difficult to explain; it is clear that whatever alkali is added the free base in the solution can only be ammonia, and it is probable that its basic properties are so reduced by the presence of the ammonium salt (compare the use of ammonium chloride in analysis) that it is no longer able to promote isomeric change. In presence of a trace of sodium ethoxide, the solubility of the sulphonamide in alcohol showed a marked increase from 11.6 to 13.6 per cent.

in the ratio 0.853 : 1. Although this value is subject to a correction for the influence of the α' - on the solubility of the α -compound, it is probable that the introduction of negative groups in the series :



is accompanied by a progressive increase in the proportion of the α' -form.

Acetyl- α -bromocamphor- π -sulphonamide. — This compound was prepared by boiling α -bromocamphor- π -sulphonamide with acetic anhydride to which a trace of sulphuric acid had been added. When the mixture was diluted cautiously with alcohol and water and allowed to cool, small, brilliant crystals were slowly deposited. These melted at 199° and were found on analysis to consist of an acetyl derivative of the amide (0.1126 gave 0.0602 AgBr ; Br = 22.76 ; $\text{C}_{12}\text{H}_{18}\text{O}_4\text{NBrS}$ requires Br = 22.70 per cent.) and not the anhydramide that was expected. It was noteworthy that the addition of a large bulk of water to solutions of this compound produced no immediate precipitation as in the case of the majority of camphor-compounds, crystallisation usually taking place only after the solution was cold. Solubility determinations showed no increase in the concentration of the saturated solution on the addition of alkali,* and it is therefore probable that the compound is the enolic acetyl derivative, $\text{C}_8\text{H}_{13}(\text{SO}_2\cdot\text{NH}_2) < \begin{array}{c} \text{CBr} \\ | \\ \text{C}\cdot\text{OAc} \end{array}$, and not the acetylamide,

$\text{C}_{10}\text{H}_{14}\text{BrO}\cdot\text{SO}_2\cdot\text{NHAc}$.

Measurable crystals were obtained from solutions in ethyl acetate, and gave the following figures :

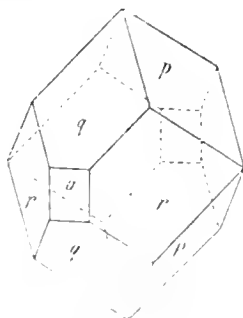


FIG. 1.

System: Orthorhombic.

Axial ratios: $a:b:c = 1.778:1:1.254$.

Forms present: $a\{100\}$, $p\{011\}$, $q\{101\}$, $r\{110\}$.

* The alkali added amounted to 0.01–0.02 per cent., and appeared to increase the density by about 0.001.

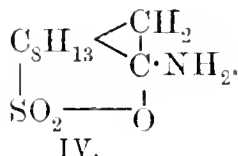
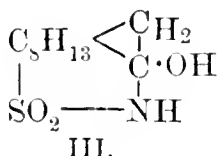
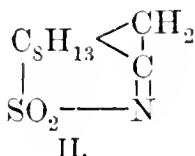
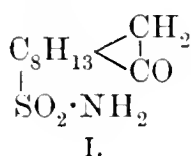
Angles measured :

<i>rp</i> 110 : 011	(20)	47° 9'	(47° 4')	<i>pq</i> 011 : 101	(20)	59° 20½'	—
<i>rr</i> 110 : 110	(2)	58° 40'	(58° 42')	<i>pp</i> 011 : 011	(6)	77° 12'	(77° 9')
<i>aq</i> 100 : 101	(12)	54° 46'	(54° 49')	<i>qq</i> 101 : 101	(6)	70° 27'	(70° 21')
<i>rq</i> 110 : 101	(21)	73° 36'	—	<i>pp</i> 011 : 011	(6)	102° 48'	(102° 51')
<i>ar</i> 100 : 110	(4)	60° 40'	(60° 39')	<i>pa</i> 011 : 100	(4)	89° 59'	(90° 0')

II. *Derivatives of Camphor-β-sulphonic Acid.*

The isomerism of the β-sulphonic derivatives of camphor presents a far more complex problem than that of the π-derivatives, on account of the readiness with which ring-formation takes place between the β- and α-positions (compare Armstrong and Lowry, *Trans.*, 1902, 81, 1441; Forster, *Trans.*, 1902, 81, 264).

Thus, in the case of the amides there may be formed in addition to the normal amide I and its anhydramide II, a lactam III and a lactone IV.



The simple sulphonamides yield either amide or anhydramide forms I and II, but there is evidence to show that the anilides may exist as hydroxylic lactams III and the piperidides as lactonic compounds IV. In the case of the α-bromo- and α-chloro-sulphonic compounds, each of these types may exist in stereoisomeric α- and α'-forms; in the case of the potassium salts which do not appear to form lactones this is probably the only isomerism which exists. The observations made with each type of compound may now be described.

1. *The Potassium Salts.*

The potassium salts of α-bromo- and α-chloro-camphor-β-sulphonic acids, unlike the ammonium salt referred to above, both showed a marked increase in solubility on the addition of a trace of ammonia to the saturated aqueous solution. In the case of the α-bromo-salt, which showed an increase of solubility from 26.6 to 32.3 per cent., experiments were made in order to ascertain the probable influence of the α'-salt on the solubility of the α-isomeride. The solubility of the αβ-salt was therefore also determined in solutions which already contained 6.40 and 6.50 per cent. of the απ-isomeride; in each case, the increase in concentration was greater than that due to the added π-salt, the total concentration of solute being 33.45 and 33.80 per cent. and the increase 6.9 and 7.2 per cent. respectively.

Thus, of the observed increase in concentration, only about eleven-twelfths is to be attributed to the added isomeride, the remaining one-twelfth being due to the increased solubility of the α -salt. If the same correction be applied in order to allow for the influence of the $\alpha'\beta$ - on the solubility of the $\alpha\beta$ -salt, it is probable that the solubility ratio 0.817 represents a proportion 0.832, or 83 per cent. of the α -salt in the solution. In the case of the chloro-salt, the solubility increases from 17.9 to 20 per cent., ratio 0.890, and there is perhaps 90 per cent. of the α -salt in the solution.

It will be noticed that in each case the increased concentration resulting from the addition of alkali is accompanied by a decrease in the rotatory power of the solution; the products of isomeric change are thus evidently laevorotatory.

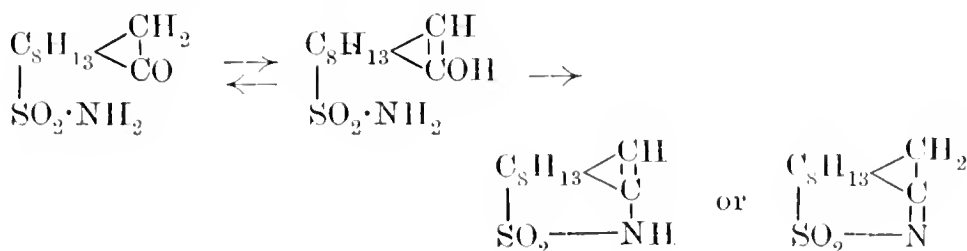
It may further be pointed out that the increased solubility now observed in these salts affords the clearest proof which has yet been obtained that the sulpho-group in the Reychler series of acids does not occupy either of the α -positions, and that the formation of β -bromo-camphor from camphorsulphobromide does not depend on a transference of bromine from an α - to the β -position (Trans., 1902, **81**, 1445).

2. *Amides and Anhydramides.*

In the paper in which his camphor sulphonic acid was first described (*Bull. Soc. chim.*, 1898, iii, **19**, 120), Reychler stated that two amides were formed by the action of ammonia on the sulphochloride. These were subsequently shown to be convertible under the action of hydrobromic acid, and were at first thought to be stereoisomerides (Armstrong and Lowry, Proc., 1901, **17**, 182), but it was subsequently shown by analysis that, although both compounds crystallise unchanged from acetic anhydride, the substance of higher melting point is actually an anhydramide formed by the removal of a molecule of water from the amide (Armstrong and Lowry, Trans., 1902, **81**, 1444). The solubility determinations recorded in the table disclosed the remarkable fact that camphor sulphonamide, although thus not affected by boiling with acetic anhydride, is rapidly and completely dehydrated by $N/500$ NaOEt in a cold alcoholic solution, a quantitative conversion into the anhydramide being effected in the course of a few hours at 20°. This was shown not only by the changed melting point of the solid, but also by the complete identity of the alkaline solutions; the slight increase produced by the alkali in the concentration of the saturated solution of the anhydramide is not due to any reverse action, but may be attributed wholly to the sodium ethoxide which was added.

This method of producing the anhydramide is very suggestive.

Lapworth has shown (Trans., 1904, 85, 30) that the velocity of bromination of ketones is directly dependent on the rate at which the ketone is converted during the experiment into the enolic isomeride. The present experiments show clearly that the conversion of camphorsulphonamide into the anhydramide is not a mere case of dehydration, but probably proceeds by means of an intermediate enolic form, the formation of which is favoured by the addition of alkalis, and to a less extent by the addition of acids.



In the case of the π -amide, acetic anhydride in the presence of acid actually causes the action to proceed as far as the formation of an enolic acetate, but the $-\text{SO}_2 \cdot \text{NH}_2$ group is too far removed to take part in the condensation.

No such abnormal behaviour was observed in the case of the β -sulphonamides derived from α -chloro- and α -bromo-camphor. These showed, on the addition of alkali, a regular increase of solubility, comparable with, though somewhat larger than, that observed in the case of bromocamphor- π -sulphonamide. No separation of anhydramide took place from the solutions, and there is no evidence to show that the solutions contain anything but the stereoisomeric α - and α' -halogen-sulphonamides.

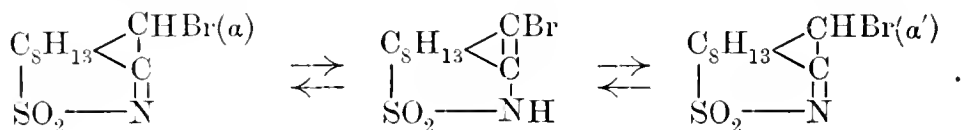
In the case of the α -bromo- β -sulphonamide, experiments were made to determine the probable influence on its solubility of the α' -isomeride in the solution. Two series of measurements were made of the solubility of the β -sulphonamide in alcohol, which already contained 1 per cent. of the isomeric π -sulphonamide; in each case, the solubility was raised to 3.10 per cent., an increase of 1.10 per cent., of which 1 per cent., or ten-elevenths of the whole, was due to the added π -sulphonamide and 0.10 per cent., or one-eleventh, to the increased solubility of the β -sulphonamide. In this case, therefore, in spite of the small solubility of the substance, there is a slight increase of solubility in presence of an isomeride. If the same correction be applied to the solubility of α -bromocamphor- β -sulphonamide in presence of the α' -isomeride, the solubility ratio 0.641 would represent a proportion 0.673, or approximately two-thirds of the α -form in the solution. In the case of the α -chlorosulphonamide, the solubility ratio 0.721 probably corresponds to a proportion 0.74 to 0.75, or roughly three-quarters of the α -form in the solution.

A long series of experiments showed that a small but definite increase of solubility is brought about by the action of alkali on the anhydramides derived from α -chlorocamphor and from α -bromocamphor; in the former case, the solubility increases from 1.28 to 1.56 per cent. in the ratio 0.820 : 1, and in the latter case from 2.51 to 2.71 per cent. in the ratio 0.926 : 1. The displacement of the ketonic oxygen by nitrogen therefore does not prevent isomeric change, although it greatly reduces the proportion of the isomeride which is formed in the solution. No increase of solubility was observed in the simple

anhydramide, $\begin{array}{c} \text{C}_8\text{H}_{13} \diagdown \text{CH}_2 \\ | \quad | \\ \text{SO}_2 \text{---} \text{C} \\ | \\ \text{N} \end{array}$, nor in the dibromoanhydramide,

$\begin{array}{c} \text{C}_8\text{H}_{13} \diagdown \text{CBr}_2 \\ | \quad | \\ \text{SO}_2 \text{---} \text{C} \\ | \\ \text{N} \end{array}$, and the increase now recorded must therefore be ascribed, as in previous cases, to a reversible stereoisomeric change.

It may be noted that, in the case of the monohalogen compounds, an intermediate isomeride of the enolic type is still possible, thus :



3. Anilides.

The anilides of this series were examined in the hope that, since direct anhydramide formation is no longer possible, they would exhibit the simple stereoisomeric change characteristic, for instance, of α -bromocamphor- π -sulphonamide. Preliminary experiments showed that the anilides were too soluble readily to be purified or used for solubility measurements. *p*-Bromoanilides were therefore prepared from α -bromo- and α -chloro-camphorsulphonic acids. It was accidentally discovered that these were soluble in alkalis, a property which was shared by the simple anilides derived from α -bromo- and from α -chloro-camphor, but not to any marked extent by the anilide or *p*-bromo-anilide derived from camphor itself. The alkaline solutions are quite stable, but the anilides are precipitated as a curdy mass on the addition of acids. This solubility in alkalis appears to be an altogether exceptional property, and is best explained by supposing that the α -substituted anilides are capable of yielding sodium salts derived from the hydroxylic lactam :



It is not easy to decide whether the anilides are themselves lactams or not.

(1) No evidence has been obtained of mutarotation in freshly-prepared solutions of the anilides, nor after the addition of acetic acid to an alcoholic solution of the sodium salt; it is therefore probable that the solution contains only a single form of the substance and not a mixture of isomerides in equilibrium.

(2) The marked difference in rotatory power between the anilide and its sodium salt suggests that they are perhaps differently constituted, the sodium salt only having the lactam structure. A solution of chlorocamphor-*p*-bromoanilide gave $[\alpha]_D +73.6^\circ$ in neutral solution, $+39.5^\circ$ in presence of 0.8 equivalents of sodium ethoxide, and $+29.2^\circ$ only in presence of an excess, 1.3 equivalents of alkali.

(3) The fact that the camphorsulphonanilides do not yield sodium salts supports the view that the anilides are not themselves lactams; it is clear that ring-formation does not take place readily, and it is therefore unlikely that the α -substituted anilides should, in the absence of alkalis, pass spontaneously into the lactam form.

(4) Although soluble to a considerable extent in alkalis, the anilides dissolve only slowly, and behave as if the dissolution involved some change beyond the mere neutralisation of an acid by a base; their behaviour suggests, in fact, that they are pseudo-acids (Hantzsch), that is, neutral compounds which only become acid after undergoing isomeric change.

(5) The *p*-bromoanilides derived from α -bromo- and from α -chloro-camphor do not show any increase of solubility on the addition of a trace of alkali. This might be attributed to the neutralisation of the alkali by the anilide, in which case the anilides might be compared with the sulphonic acids, which undergo change only in presence of a quantity of alkali in excess of that required for neutralisation. The observations recorded above show, however, that no marked alteration of rotatory power follows the addition of an excess of alkali to the sodium salt. The case appears, therefore, to be similar to that of nitrocamphor, in which the formation of a salt affords an alternative to, and thus effectually prevents, enolisation.

In view of the fact that the anilides derived from α -bromo- and α -chloro-camphor show no increase of solubility in presence of alkalis, it is somewhat remarkable that those derived from camphor show a distinct change. Although the increase in concentration amounts only to 0.1 per cent., it was clearly established by some thirty-five measurements of the solubility of the anilide and of the *p*-bromoanilide. Various possibilities of isomeric change might be suggested, but there is not sufficient evidence to permit of any definite conclusion as to the nature of the change which takes place.

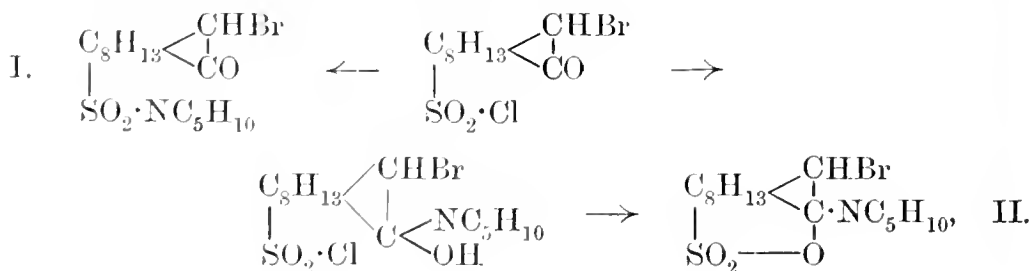
α -Chlorocamphor- β -sulphonanilide melts at 97° , has specific rotation $[\alpha]_D +79^\circ$ (in alcohol), and is reduced by zinc dust and acetic acid to camphorsulphonanilide, melting at 119° . The partially purified material was decolorised by dissolving in alkali, filtering, and precipitating with acids. Like the α -bromo-compound, it crystallises from alcohol in a dense mass of felted needles.

α -Chlorocamphor- β -sulpho- p -bromoanilide (0.2145 gave 0.1686 AgCl + AgBr, Cl + Br = 27.39; $C_{16}H_{19}O_3NClBrS$ requires Cl + Br = 27.44 per cent.) melts at 115° . It was purified by dissolving in alkali and precipitating with acid; the curdy mass was obtained in a crystalline form by covering it with cold methyl alcohol, in which it quickly dissolved and separated again in crystals in the course of a few minutes. It was further purified by crystallising from alcohol, from which it separates in rectangular tablets with truncated edges. It was reduced by zinc dust and acetic acid to the camphor- β -sulpho- p -bromoanilide melting at 167° .

α -Bromocamphor- β -sulpho- p -bromoanilide (0.1625 gave 0.1321 AgBr, Br = 34.6; $C_{16}H_{19}O_3NBr_2S$ requires Br = 34.4 per cent.), prepared from bromocamphorsulphochloride and p -bromoaniline and from bromocamphorsulphonanilide and bromine, melts at 95° and resembles the preceding compound.

4. Piperidides.

The existence of isomeric piperidides derived from camphorsulphonic acid has already been clearly established (Armstrong and Lowry, Trans., 1902, 81, 1449), but at that time only a single α -bromopiperidide could be prepared, namely, that derived from the camphor-piperidide of high melting point. In the course of the present investigation it was found that when the α -bromopiperidide was prepared by the Schotten-Baumann method, using aqueous piperidine instead of an ethereal solution, an isomeric compound of low melting point was produced. It is probable that in the Schotten-Baumann method of preparation the interaction proceeds normally, giving rise to the true piperidide I; in ethereal solution, the piperidine probably combines with the carbonyl group, hydrogen chloride is subsequently eliminated, and the piperido-lactone II is produced.



The conclusion thus arrived at, that the compounds of low melting point are the true piperidides, whilst the high melting compounds are piperido-lactones, is in accord with the rise of melting point which accompanies ring formation when the amides are converted into anhydramides.

Both bromopiperidides show a marked increase of solubility in presence of alkalis, the ratio of the initial to the final solubility being 2:3 approximately in each case. This increase, which does not occur in the case of camphor piperido-lactone, must be attributed to stereoisomeric change, and probably involves the opening of the lactone ring. It should be noted that whilst both bromopiperidides are readily converted into isodynamic stereoisomerides, they are not convertible into one another either by the action of acids or of alkalis. Owing to the small quantity of pure material available, the densities and rotatory powers of the saturated solutions were not determined.

Camphor- β -sulphopiperidide, provisionally described (*loc. cit.*) as *iso-camphorsulphopiperidide* (?), melts at 56°.

Camphor- β -sulphopiperidolactone, provisionally described as *camphor-sulphopiperidide* (?), melts at 140°.

α -Bromocamphor- β -sulphopiperidide (0.2958 gave 0.1479 AgBr, Br = 21.28; $C_{15}H_{24}O_3NBrS$ requires Br = 21.14 per cent.) melts at 75° and crystallises from alcohol, or, when pure, from light petroleum. From the latter solvent it separates in small, orthorhombic prisms, $a:b:c = 1.112:1:1.095$.

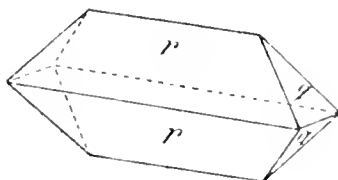


FIG. 2.

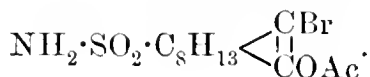
<i>rr</i> 101 : 10 $\bar{1}$	(12)	90°52'	—	<i>qq</i> 011 : 01 $\bar{1}$	(6)	84°47'	—
<i>rr</i> 101 : $\bar{1}$ 01	(12)	89° 9'	(89° 8')	<i>qq</i> 011 : 0 $\bar{1}$ 1	(6)	95°15'	(95°13')
<i>qr</i> 011 : 101	(2)	61°30'	(61°18')	<i>rq</i> 101 : 0 $\bar{1}$ 1	(2)	118°41'	(118°42')

α -Bromocamphor- β -sulphopiperidolactone, formerly described as *α -bromocamphorsulphopiperidide*, melts at 123°.

Summary.—(1) In continuation of the work described in the previous paper, measurements have been made of the solubility of twenty sulphonic derivatives of camphor in neutral and alkaline solutions.

(2) The amide of bromocamphor- π -sulphonic acid, an acid which has been shown by Kipping to undergo stereoisomeric change in presence of a trace of free alkali, increases in solubility from 11.6 to 13.6 per

cent. in the ratio 0·853:1 when alkali is added to the alcoholic solution. An acetyl derivative prepared from the sulphonamide shows no increase, and is therefore formulated as the enolic acetate,

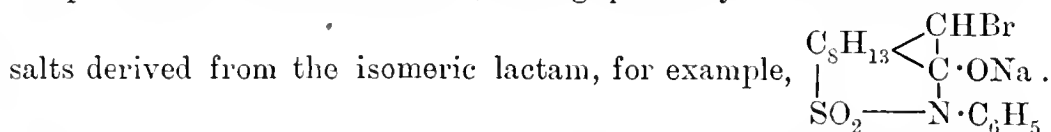


(3) The potassium salts of α -bromocamphor- and α -chlorocamphor- β -sulphonic acids show a marked increase of solubility when ammonia is added to the aqueous solutions, and therefore (like the isomeric π -acids) exist in stereoisomeric forms; the α' -salts are levorotatory.

(4) In presence of a trace of sodium ethoxide camphor- β -sulphonamide is converted quantitatively in cold alcoholic solution into the anhydramide; this is remarkable, as the amide crystallises unchanged from boiling acetic anhydride.

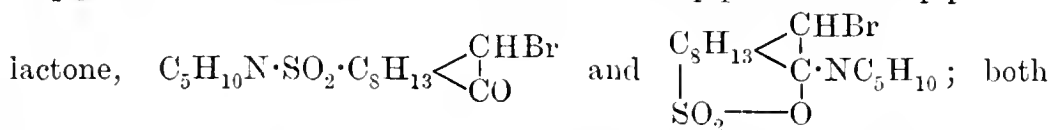
(5) The β -sulphonamides of bromocamphor and chlorocamphor, like the π -compound, show an increased solubility in alkaline solution owing to stereoisomeric change, but are not converted into anhydramides.

(6) The β -sulphonanilides derived from bromocamphor and chlorocamphor are soluble in alkalis, owing probably to the formation of



Owing to the formation of these compounds, the anilides are not converted into stereoisomerides by the action of alkalis. Three new anilides are described.

(7) Isomeric piperidides derived from bromocamphor- β -sulphonic acid are described, corresponding with those prepared from camphor-sulphonic acid. These are formulated as the piperidide and piperido-



compounds undergo stereoisomeric change in presence of alkalis.

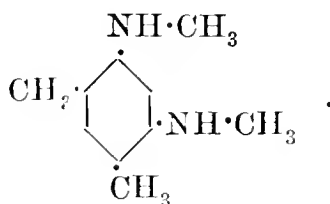
WESTMINSTER TRAINING COLLEGE,
LONDON, S.W.

CVIII.—*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part V.*
s-Dimethyl-4 : 6-diamino-*m*-xylene.

By GILBERT THOMAS MORGAN and ARTHUR CLAYTON, B.Sc.

THE experiments described in the earlier communications of this series have shown that the formation of aminoazo-compounds can occur with primary aromatic meta-diamines containing substituents in both the para-positions with respect to the amino-groups, although the reaction takes place less readily than when one of these para-positions is still unoccupied (Trans., 1902, 81, 86 ; 1905, 87, 935, 944).

One of the authors having found that the complete alkylation of the two amino-groups in a dipara-substituted meta-diamine inhibits the production of an azo-derivative (Trans., 1902, 81, 656), the investigation was extended to the partially alkylated derivatives in order to ascertain what effect the progressive alkylation of these bases has on the course of the azo-condensation. In the present instance, the case of a symmetrically dialkylated meta-diamine has been examined, the base chosen for this purpose being *s*-dimethyl-4 : 6-diamino-*m*-xylene :



4 : 6-Diamino-*m*-xylene, the starting point of this research, was prepared in the manner formerly indicated (Trans., 1902, 81, 92) and transformed by means of the Schotten-Baumann reaction into *s*-dibenzenesulphonyl-4 : 6-diamino-*m*-xylene,



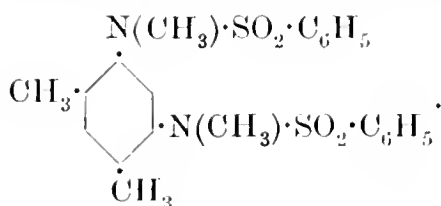
which, when crystallised repeatedly from dilute alcohol or acetone, separated in prismatic needles melting at 176°.

0.4165 gave 25.3 c.c. nitrogen at 21° and 764 mm. N = 6.95.

$\text{C}_{20}\text{H}_{20}\text{O}_4\text{N}_2\text{S}_2$ requires N = 6.73 per cent.

This compound is readily soluble in aqueous alkalis, and is precipitated from solution by dilute acetic acid.

s-Dibenzenesulphonyldimethyl-4 : 6-diamino-*m*-xylene,



The foregoing compound was readily methylated when boiled for six hours in alcoholic solution with sodium hydroxide (2.5 mols.) and methyl iodide (3 mols.), the latter reagent being added gradually. The clear solution thus obtained when left overnight furnished a deposit of hard, nodular crystals; when recrystallised from alcohol, the compound separated in colourless crystals and melted at 196—197°.

0.2857 gave 0.3115 BaSO₄. S = 14.97.

0.3401 „ 20.0 c.c. nitrogen at 23° and 764 mm. N = 6.66.

C₂₂H₂₄O₄N₂S₂ requires S = 14.41; N = 6.31 per cent.

This dimethylated sulphonyl derivative was quite insoluble in aqueous alkalis, and the amount which separated from the alcoholic solution used in the methylation was 90—95 per cent. of the calculated quantity.

s-Dimethyl-4 : 6-diamino-*m*-xylene.

After many unsuccessful attempts to hydrolyse the preceding compound with alcoholic hydrochloric acid, it was found that this reaction was most readily effected by heating the substance with concentrated hydrochloric acid (15 parts) in sealed tubes at 160° for five hours. The temperature requires careful regulation, as at 180° decomposition sets in. In these experiments it is important to use highly purified dibenzenesulphonyldimethyl-4 : 6-diamino-*m*-xylene, otherwise tarry by-products are formed even at temperatures lower than that required to effect the hydrolysis. The resulting solution was concentrated and rendered ammoniacal, when *s*-dimethyl-4 : 6-diamino-*m*-xylene was precipitated, the yield being about 60 per cent. of the calculated amount. After crystallisation from light petroleum (b. p. 60—80°), the new diamine was obtained in the form of colourless plates melting at 100—101°. A mixture of this substance with the original 4 : 6-diamino-*m*-xylene (m. p. 104°) melted at about 80°. A complete analysis confirmed the composition of the dimethylated diamine.

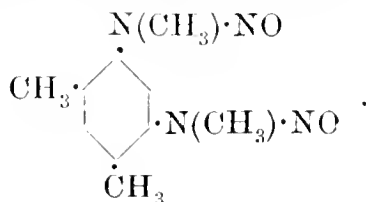
0.1758 gave 0.4712 CO₂ and 0.1572 H₂O. C = 73.07; H = 9.94.

0.1731 „ 25.5 c.c. nitrogen at 15° and 750 mm. N = 17.03.

C₁₀H₁₆N₂ requires C = 73.17; H = 9.76; N = 17.07 per cent.

The new diamine dissolved readily in ether, and the solution slowly deposited colourless, flattened, rectangular prisms, often of considerable size. When carefully recrystallised, the dried base was fairly permanent, and did not become appreciably coloured on exposure under atmospheric conditions. Impure specimens, however, rapidly assumed a green tint, and when subsequently extracted with light petroleum the colouring matter was left as an insoluble green powder.

s-Dimethyl-4 : 6-dinitrosoamino-*m*-xylene,



In order to obtain further evidence for the structural formula ascribed to the foregoing diamine, its hydrochloride was subjected to the action of nitrous acid. When aqueous sodium nitrite (2.5 mols.) was slowly added to a solution of the base in excess of cold dilute hydrochloric acid, a white, pulverulent precipitate separated, which was quite insoluble in aqueous solutions of the mineral acids. This product crystallised readily from alcohol or light petroleum (b. p. 60—80°) and separated in aggregates of very pale yellow, transparent, rectangular plates melting at 76—77°.

0.1298 gave 28.8 c.c. nitrogen at 20° and 758 mm. $N = 25.32$.

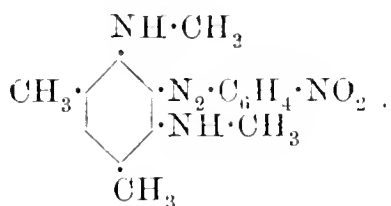
$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_4$ requires $N = 25.22$ per cent.

s-Dimethyl-4 : 6-dinitrosoamino-*m*-xylene gave intense colorations in all the phases of the Liebermann reaction, thus behaving as a typical nitrosoamine. It is noteworthy that this dinitrosoamine, which contains substituent (CH_3) groups in both para-positions to the aminic nitrogen, is very nearly colourless, whereas its lower homologues containing free para-positions are generally described as coloured compounds, the prevailing colour being yellow.

Action of Diazo-compounds on s-Dimethyl-4 : 6-diamino-*m*-xylene.

When a piece of cotton cloth impregnated with diazotised primuline was immersed in a cold dilute aqueous solution of *s*-dimethyl-4 : 6-diamino-*m*-xylene and kept in the dark, an ingrain azo-colour was slowly produced, the fabric acquiring a reddish-brown shade. This indication of the production of an azo-derivative was confirmed by the following experiment.

One molecular proportion of *p*-nitraniline was dissolved in a cooled mixture of concentrated acetic and hydrochloric acids and carefully diazotised with the calculated amount of aqueous sodium nitrite (20 per cent.). The diazo-solution, after dilution with ice-cold water, was poured into a cold solution of *s*-dimethyl-4:6-diamino-*m*-xylene in dilute hydrochloric acid. No change occurred until excess of aqueous sodium acetate was added, when a yellow precipitate appeared, which rapidly assumed a brownish-red colour. After eight hours, this precipitate was collected, washed with water, dried on porous tile, and then repeatedly extracted with benzene. These extracts, when concentrated, yielded a crystalline substance, which, when dry, had a reddish-grey colour. This product, when recrystallised from benzene, gave dark red needles mixed with a pale red, powdery substance. The dark red crystals were separated mechanically and found to melt at 218°. The light red compound, which also melted at 218° when dissolved in benzene, slowly separated in the darker form. These two substances do not depress each other's melting points, and are therefore modifications of the same chemical compound, which has the composition and properties of *p*-nitrobenzene-5-azodimethyl-4:6-diamino-*m*-xylene,



0.0895 gave 16.8 c.c. nitrogen at 20° and 770 mm. N = 21.76.

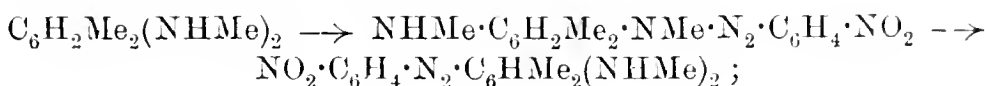
$\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}_5$ requires N = 22.36 per cent.

This azo-derivative developed a reddish-orange coloration with cold concentrated sulphuric acid, in this respect resembling the other *o*-aminoazo-derivatives of the meta-diamine series.

The yield of the product in this instance was very small, being only about 10 per cent. calculated on the weight of the diamine.

The residue insoluble in benzene when heated with concentrated hydrochloric acid in the volumeter evolved nitrogen, the amount of gas corresponding with about 25 per cent. of a diazoamino-compound.

The light yellow colour of the original precipitate produced by the addition of sodium acetate to the mixed solutions of diamine and diazonium salt also points to the initial production of a diazoamine. In all probability the reaction involving the formation of the azo-derivative takes the following course:



this change, however, is accompanied by the formation of ill-defined by-products.

Interaction of p-Nitrobenzenediazonium Chloride and 5-Bromo-as(4)-dimethyl-2 : 4-diaminotoluene.

The product of this interaction was previously stated (Trans., 1905, 87, 946) to contain a diazoamine and an aminoazo-compound. Further evidence has now been obtained by extracting the dried mass with benzene and recrystallising the more soluble portion.

After three fractional crystallisations from this solvent, a compound was obtained crystallising in small, reddish-brown leaflets and melting with decomposition at 162° , which gave the following results on analysis :

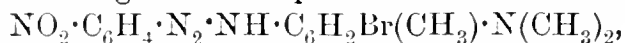
0.0970 gave 16.4 c.c. nitrogen at 20° and 769 mm. $N = 19.5$.

0.0945 „ 0.0464 AgBr. $Br = 20.84$.

$C_{15}H_{16}O_2N_5Br$ requires $N = 18.5$; $Br = 21.16$ per cent.

These data corresponded with an azo-compound having the formula $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6HBr(CH_3)[N(CH_3)_2] \cdot NH_2$, but the amount at our disposal was too small for more detailed examination. With cold concentrated sulphuric acid the substance developed a brownish-orange coloration.

The residue from the benzene extracts had a light brown colour and gave the magenta coloration with alcoholic potash characteristic of a *p*-nitrodiazoamine, but it was not found possible to obtain this compound in a crystalline form. A-bromine estimation of the crude uncrystallised product showed that this contained an amount of the halogen approximating to that required for a diazoamine,



derived from *p*-nitrobenzenediazonium chloride and 5-bromo-*as*(4)-dimethyl-2 : 4-diamino-*m*-xylene.

These results show that the dimethylation—both symmetrical and unsymmetrical—of a dipara-substituted meta-diamine greatly hinders, but does not entirely prevent, the introduction of a diazo-residue into the aromatic nucleus of the diamine, and in both cases there was evidence of the formation of a diazoamine.

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CIX.—*Ammonium Selenate and the Question of Isodimorphism in the Alkali Series.*

By ALFRED EDWIN HOWARD TUTTON, M.A., D.Sc. (Oxon.), F.R.S.

AMMONIUM SELENATE was not included in the scope of the author's last communication (Trans., 1905, 87, 1188) on the topic parameters of the alkali sulphates and selenates, inasmuch as it had not been found possible to prepare rhombic crystals of this salt isomorphous with those of ammonium sulphate and the sulphates and selenates of potassium, rubidium, and caesium. In the year 1862, Victor von Lang published (*Sitzungsber. K. Akad. Wiss. Wien*, 45, ii, 109) a description of rhombic crystals of ammonium selenate, prepared by von Hauer, isomorphous with those of ammonium sulphate, and mentioned also some thin needles having a prism angle of $42^{\circ}55'$, which were optically different from the rhombic crystals.

Fig. 1 is a copy of von Lang's drawing of the rhombic crystals with modernised symbols.

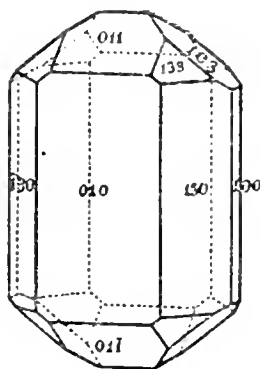


FIG. 1.

Ten years later, Topsøe (*Arch. des Sciences phys. et nat., Genève*, 1872, 45, 80) prepared the salt by the saturation of selenic acid with ammonia, and, by allowing the solution to evaporate spontaneously, obtained prismatic and tabular crystals belonging to the monoclinic system, but no rhombic crystals as described by von Lang. He concluded, therefore, that ammonium selenate is dimorphous, but that the conditions for the production of the rhombic form are unknown.

The possibility of isodimorphism in the various series of salts of potassium, rubidium, caesium, and ammonium has recently been discussed by Gossner (*Zeit. Kryst. Min.*, 1905, 40, 69). It frequently happens that the corresponding salts of the same acid crystallise differently under ordinary conditions. Thus, Gossner had already

shown (*ibid.*, 1904, 39, 381) that ammonium hydrogen sulphate and potassium hydrogen sulphate crystallise in quite different forms of the rhombic system. The change or gap occurs between the potassium and the rubidium salts in the double uranyl nitrates investigated by Sachs (*ibid.*, 1904, 38, 496), the potassium salt being rhombic and the rubidium and caesium salts rhombohedral, whilst it occurs between the rubidium and caesium salts in the double chlorides with ferric chloride investigated by Gossner in the memoir now under discussion. In every case, however, in which the members of the series on both sides of the gap have been crystallised from mixed solutions, the missing form has been discovered in the mixed crystals. Gossner concludes, therefore, that "die entsprechenden Salze von NH_4 , K, Rb, Cs bilden immer eine isomorphe Gruppe, zeigen jedoch auffallend häufig die Erscheinung der Isodimorphie. In reinem Zustande ist meist nur die eine Modification für ein Salz bekannt; in isomorphen Mischungen ist jedoch die fehlende zweite Modification immer nachzuweisen."

Preparation of the Pure Salt and Crystallisation under Different Conditions.

The salt was prepared by saturating pure selenic acid obtained from Merck, diluted with an equal bulk of water and contained in the three bulbs of a U-absorption tube, with ammonia gas obtained by gently warming an ammonia solution of 0.880 sp. gr. The reaction is accompanied by considerable evolution of heat. The salt is nearly twice as soluble in water as ammonium sulphate, and is, indeed, remarkably deliquescent; moreover, the saturated solution is highly viscous.

Four different preparations were made of about 25 grams of the pure salt in each case. The filtered solutions were concentrated to saturation or supersaturation and allowed to crystallise, either as a whole or after subdivision, under the following different conditions: (1) spontaneously in the open air of the laboratory; (2) in a desiccator over concentrated sulphuric acid at the ordinary atmospheric pressure; (3) over concentrated sulphuric acid in a vacuum; (4) at a warm summer temperature under the three previous conditions; (5) similarly, at a cold winter temperature; (6) at the temperature of a freezing mixture of ice and salt; (7) at a temperature of 70° after saturation at 100° ; (8) at the ordinary temperature after dropping into the solution a crystal of ammonium sulphate.

In every instance, monoclinic crystals only were deposited of the characters detailed in the latter portion of this communication and

corresponding to the brief description of Topsøe. Determinations of selenium, by reduction with hydrochloric acid and sulphur dioxide, proved that they consisted of pure anhydrous neutral ammonium selenate. In case (8), the crystal of ammonium sulphate dissolved.

The effect of employing a different solvent was also tried. Alcohol and acetone do not appreciably dissolve the salt, but glacial acetic acid is a good solvent. From this solution there were only monoclinic crystals deposited, of similar habit and angles to those deposited from water.

Hence all efforts to obtain the rhombic variety of ammonium selenate failed.

Mixed Crystals.

(a) *Ammonium Selenate and Sulphate*.—Two solutions were prepared, containing equal molecular quantities of the two salts in one case and two molecular proportions of the selenate to one of the sulphate in the other. In both instances, rhombic crystals resembling those of the sulphate were deposited on evaporation or cooling, and in the case of the solution containing equal molecular equivalents these were the sole product observed. In the case of the other solution, however, monoclinic crystals resembling those of ammonium selenate were also deposited. The composition of the crystals of several crops derived from each of the two solutions was investigated by the immersion specific gravity method, using as liquid a mixture of methylene iodide and benzene.

The specific gravity of ammonium sulphate crystals at $20^{\circ}/4^{\circ}$ has been shown by the author to be 1.772 (Trans., 1905, 87, 1187). That of pure ammonium selenate (monoclinic) at the same temperature will be shown later in this communication to be 2.194.

Rhombic crystals from solution of equal molecules.

Sp. gr. at $20^{\circ}/4^{\circ}$: Crop 1, 1.813. Crop 2, 1.822.

These values correspond to crystals containing respectively 9.7 and 11.8 per cent. of ammonium selenate.

The crystals of these and several other crops were goniometrically investigated and found to resemble strongly those of ammonium sulphate, the angles being within $3'$ of those for that salt.

Crystals from solution of $(\text{NH}_4)_2\text{SO}_4 + 2(\text{NH}_4)_2\text{SeO}_4$.

The first crop of crystals was not well formed, but the second was quite good, and the two kinds of crystal deposited gave the following densities:

(1) Rhombic tabular crystals, similar in character to those derived from the solution of equal molecules, sp. gr. at $20^{\circ}/4' = 1.840$.

(2) Monoclinic crystals, elongated prisms like those illustrated later in Fig. 4, sp. gr. at $20^{\circ}/4^{\circ} = 2.066$.

These densities correspond to crystals containing respectively 16.1 and 69.7 per cent. of ammonium selenate.

Four successive crops were investigated, and always found to consist of rhombic plates and bundles of radiating monoclinic prisms showing angles very close to those of pure ammonium selenate.

Twins were also observed of the kind described later for the pure salt.

(b) *Ammonium and Potassium Selenates*.—A solution of equal molecular proportions deposited only rhombic mixed crystals of the type of those of potassium selenate and showing similar angles: sp. gr. at $20^{\circ}/4^{\circ} = 2.793$. As that of potassium selenate is 3.067, the crystals apparently contained 31.4 per cent. of ammonium selenate.

(c) *Ammonium and Rubidium Selenates*.—A solution of equal molecular proportions of these salts also deposited only rhombic mixed crystals similar in type and angles to those of rubidium selenate: sp. gr. at $20^{\circ}/4^{\circ} = 3.160$, corresponding to 43.4 per cent. content of ammonium selenate (sp. gr. of pure $\text{Rb}_2\text{SeO}_4 = 3.902$). A second solution containing two molecular proportions of ammonium selenate and one of rubidium selenate also yielded only rhombic crystals. Two crops were examined: the first had a sp. gr. of 2.891, corresponding to 59.19 per cent. of ammonium selenate, and the second had a sp. gr. of 2.858, corresponding to 61.12 per cent. The latter mixed crystals were of perfect form, rectangular tables parallel to $b\{010\}$, bevelled by faces of the prisms $p\{110\}$ and $p'\{130\}$, and the domes $q\{011\}$ and $q'\{021\}$; they were the richest in ammonium selenate of any rhombic crystals obtained. The ease with which these two salts crystallise together is doubtless due to the close similarity which has in general been shown by the author to exist between the structure of ammonium and rubidium salts, as indicated by their closely approximating topic axes.

Reinvestigation of von Lang's Crystals.

Having had the good fortune to make the personal acquaintance of Prof. von Lang, the author communicated to him the main result of the investigation. Happily the identical crystals investigated in 1862 had been carefully preserved, and Prof. von Lang most generously

forwarded them from Vienna to the author. They were contained in a small tube, plugged with cotton wool, and closed by a tightly fitting cork. Their condition after forty-four years was still sufficiently good to enable most valuable observations to be made with them, although there was not a large enough quantity to enable any to be used for analysis. The crystals had lost many of their edges by deliquescence, but this had not gone too far to prevent reflections from being obtained from many of the faces.

The majority of the crystals corresponded precisely to the rhombic type described by Prof. von Lang, but besides these there were two or three of the thin needles to which he also refers. The best preserved of the latter and several of the rhombic type were selected for investigation. Their density was first determined by the immersion method (using methylene iodide and benzene), and afterwards they were goniometrically and optically examined. The results of the density determinations are as under :

	Sp. gr. at 20°/4°
Rhombic variety.....	2·0774
Elongated prism (needle) ...	2·1719

(Sp. gr. of pure ammonium sulphate, 1·772, and of ammonium selenate, 2·194.) Allowing for possible deterioration by time (internal deliquescence), the needle corresponded remarkably closely in density to monoclinic ammonium selenate. Subsequent goniometrical examination of it at once revealed the interesting fact that it was identical crystallographically with the monoclinic variety of Topsøe and the author. The elongated prism zone was the zone $[acm]$, which has usually been the predominating zone in the author's preparations, giving rise to long prisms. A fairly trustworthy measurement of $ac=(100):(001)$ gave the angle $64^{\circ}36'$, another of $cm=(001):(201)$ gave $68^{\circ}0'$, and a third of $am=(100):(20\bar{1})$ yielded $47^{\circ}20'$. These are sufficiently close to the author's mean values (see table on p. 1067) for these angles, $64^{\circ}31'$, $68^{\circ}27'$, and $47^{\circ}2'$, to enable the conclusion to be drawn that they are identical with the monoclinic variety. The terminal planes forming the pointed end were also adequately good to enable them to be identified as those of the monoclinic primary prism $p\{110\}$ and hemipyramid $o'\{\bar{1}11\}$. The prism angle of $42^{\circ}55'$, which von Lang states was given by the thin needle measured by him, was doubtless that of a twin prism, which the author finds to be a very common form and which has a theoretical angle of $43^{\circ}16'$.

The best crystal of the rhombic variety was a rectangular rhombic

plate, and, although deliquescence had set in to a considerable extent, measurements were obtained which proved conclusively that the tabular plane of the crystal was the brachypinacoid $b\{010\}$, that the longer edges were bevelled by faces of the prism $\{130\}$ inclined at approximately 31° , and that the shorter edges (zone at right angles to the one just referred to) were bevelled by the dome $\{011\}$ inclined at $53\frac{1}{2}^\circ$ to the tabular plane. These values are sufficient to identify the crystal with one of those measured by Prof. von Lang, and confirm the rhombic symmetry and similarity to ammonium sulphate and the other alkali sulphates and selenates. The position and angles of separation of the optic axes were determined by immersion of the crystal in oil of anise, which has nearly the same refractive index. The first median line is the normal to $c\{001\}$, and the plane of the optic axes is the tabular plane $b\{010\}$. The true angle $2V_a$ for red is $55^\circ 36'$, and for blue $58^\circ 54'$. Thus, rhombic ammonium sulphate and ammonium selenate have an identical optic axial plane, but, as Prof. von Lang says, the first and second median lines are interchanged.

As regards the composition of Prof. von Lang's crystals, the densities found for the two varieties, even allowing for considerable deterioration due to age and deliquescence, appear to indicate that the solution from which they were grown contained some admixed ammonium sulphate. If there were no deterioration, the density results would correspond to rhombic crystals containing 73 per cent. of ammonium selenate and the rest of sulphate, and to monoclinic crystals containing 95 per cent. of ammonium selenate. But this is probably an exaggeration of the degrees of impurity, as deterioration would account for part of it. The results afford, however, reasonable proof that there was some isomorphous impurity, probably ammonium sulphate, as this is the only salt of lower density in the series, and that the greater part of it was concentrated in the rhombic crystals, the strict isomorphs of the impurity. It has been shown in a preceding section of this memoir that rhombic mixed crystals can readily be obtained when 33 per cent. of a rhombic salt of the series is present along with ammonium selenate in the parent solution, and as rich as 60 per cent. in ammonium selenate when rubidium selenate is the second salt.

Monoclinic Variety of Ammonium Selenate.

An estimation of selenium in 1.0406 grams of the crystals by reduction with hydrochloric acid and sulphur dioxide gave $\text{Se} = 43.72$ per cent. The calculated percentage for $(\text{NH}_4)_2\text{SeO}_4$ is $\text{Se} = 44.16$. It was found somewhat difficult to precipitate the last trace of selenium. Topsøe also obtained 43.7.

Symmetry: Monoclinic, holohedral.

Habit: Prismatic (even acicular) along the direction of the symmetry axis or tabular parallel to the basal plane, ortho-pinacoid, or hemi-pyramid $o'\{111\}$.

Type of Structure: Pseudo-hexagonal, primary prism zone faces inclined at approximately 60° (within 1°).

Ratio of Axes: $a:b:c = 1.8900:1:1.1987$.

Axial Angle: $\beta = 64^\circ 31'$.

Forms observed: $a\{100\}$, $c\{001\}$, $m\{201\}$, $p\{110\}$, $p'\{310\}$, $o\{111\}$, $o'\{\bar{1}11\}$, $n\{\bar{3}11\}$.

Twinning: Common, on a plane perpendicular to the symmetry plane and to the normal to $c\{001\}$, the latter being the twin axis.

Cleavage: Three directions, parallel to $a\{100\}$ most perfect, $c\{001\}$ next in order of perfection, and $b\{010\}$.

The spherical projection is given in Fig. 2.

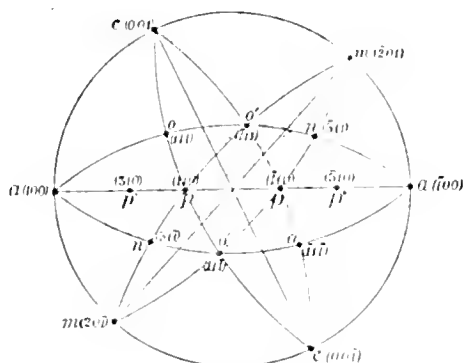


FIG. 2.

Twenty-two crystals were employed in the goniometrical work, selected from eleven different crops, some obtained from saturated solutions placed over concentrated sulphuric acid in a vacuum, and some over sulphuric acid at the ordinary pressure, whilst two were from strongly supersaturated solutions exposed to the open atmosphere. The latter method only yields good crystals on very dry days owing to the rapid deliquescence of the crystals in moist air.

The prismatic class varied from thin needles to solid blocks, such as that shown in Fig. 3, but were very commonly of the intermediate character shown in Fig. 4, with the two faces belonging to each form of the elongated zone developed to very different extents. Certain of the crops obtained in a vacuum yielded thick, tabular crystals of the kind illustrated in Fig. 5. The relative development of faces was

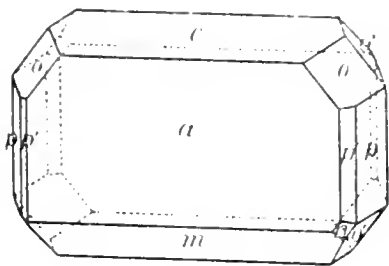


FIG. 3.

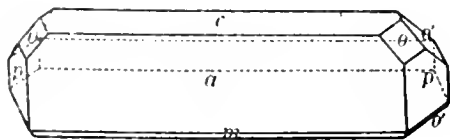


FIG. 4.

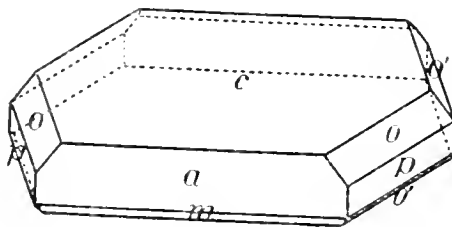


FIG. 5.

so varied that every one of the five principal forms $a\{100\}$, $c\{001\}$, $m\{201\}$, $p\{110\}$, $o'\{\bar{1}11\}$ was observed most prominently developed in turn, and often the two halves of the same crystal were differently developed.

The crystals have a brilliant, clear, waxy appearance, and are very soft. Their saturated aqueous solution is very viscous.

The results of the measurements are presented in the accompanying table.

The only angular value given by Topsøe is that for ac , which is also the angle between the oblique axes, and which he found to be $64^{\circ}27'$. The agreement affords adequate proof of the identity of the crystals.

The numerous twins are characterised by the elongated ortho-prism zone $[acm]$ showing two different angles, aa $50^{\circ}58'$ and mm $43^{\circ}16'$, on different sides of the centre, instead of the two equal angles am of $47^{\circ}7'$ of the single crystal. Also the ends of the elongated prisms show re-entrant angles, the value between the two

approximated *p*-faces of the two individuals being 25° 8' and that between the two *o*'-faces of different individuals 61° 24'. Re-entrant angles are also frequently shown along the flatter ridges of the elongated prisms, owing to thin strips of the next normal faces of each single crystal being also present. Five such twins were measured and the values observed for these four twin angles were, on the average, within 4' of the calculated values just enumerated. Fig. 6 will render the construction of the twins clearer, the plane of projection being the symmetry plane, as in the case of the spherical projection of the normal single crystals given in Fig. 2. It is as if a single crystal were cut through along a plane parallel to *c*{001} and perpendicular to the symmetry plane of projection, and one-half were then rotated for 180° about the normal to *c*{001} as twin axis.

Morphological Angles of Monoclinic Ammonium Selenate.

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.	Difference.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ cm = (001) : (\bar{2}01) \\ ma = (\bar{2}01) : (\bar{1}00) \end{array} \right.$	<div>40</div> <div>39</div> <div>31</div>	<div>64°22'—61°44'</div> <div>68 11—68 42</div> <div>46 40—47 29</div>	<div>64°31'</div> <div>68 27</div> <div>47 2</div>	<div>*</div> <div>68°22'</div> <div>47 7</div>	<div>—</div> <div>5'</div> <div>5</div>
$\left\{ \begin{array}{l} ap' = (100) : (310) \\ p'p = (310) : (110) \\ ap = (100) : (110) \\ pp = (110) : (\bar{1}10) \end{array} \right.$	<div>4</div> <div>3</div> <div>36</div> <div>13</div>	<div>29 27—29 49</div> <div>29 52—30 8</div> <div>59 23—59 56</div> <div>60 33—60 50</div>	<div>29 36</div> <div>30 0</div> <div>59 38</div> <div>60 42</div>	<div>29 38</div> <div>30 0</div> <div>*</div> <div>60 44</div>	<div>2</div> <div>0</div> <div>—</div> <div>2</div>
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oo' = (111) : (111) \\ ao' = (100) : (\bar{1}11) \\ o'n = (\bar{1}11) : (311) \\ na = (\bar{3}11) : (\bar{1}00) \\ o'a = (\bar{1}11) : (\bar{1}00) \end{array} \right.$	<div>17</div> <div>14</div> <div>29</div> <div>—</div> <div>—</div> <div>26</div>	<div>52 45—53 5</div> <div>45 6—45 29</div> <div>98 4—98 25</div> <div>—</div> <div>—</div> <div>81 35—81 58</div>	<div>52 58</div> <div>45 16</div> <div>98 14</div> <div>—</div> <div>—</div> <div>81 46</div>	<div>52 56</div> <div>45 18</div> <div>98 14</div> <div>38 2</div> <div>43 44</div> <div>81 46</div>	<div>2</div> <div>2</div> <div>0</div> <div>—</div> <div>—</div> <div>0</div>
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (111) \\ o'c = (111) : (001) \end{array} \right.$	<div>14</div> <div>14</div> <div>34</div> <div>24</div> <div>31</div>	<div>43 43—43 58</div> <div>33 20—33 43</div> <div>77 11—77 37</div> <div>43 7—43 34</div> <div>59 10—59 27</div>	<div>43 51</div> <div>33 30</div> <div>77 22</div> <div>43 19</div> <div>59 18</div>	<div>43 53</div> <div>33 33</div> <div>77 26</div> <div>43 16</div> <div>*</div>	<div>2</div> <div>3</div> <div>4</div> <div>3</div> <div>—</div>
$\left\{ \begin{array}{l} mo' = (\bar{2}01) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pn = (110) : (311) \\ nm = (311) : (\bar{2}01) \\ pm = (110) : (\bar{2}01) \end{array} \right.$	<div>29</div> <div>25</div> <div>1</div> <div>1</div> <div>23</div>	<div>55 42—55 56</div> <div>54 5—54 32</div> <div>—</div> <div>—</div> <div>69 30—70 3</div>	<div>55 50</div> <div>54 18</div> <div>34 34</div> <div>35 18</div> <div>69 52</div>	<div>55 47</div> <div>54 20</div> <div>34 35</div> <div>35 18</div> <div>69 53</div>	<div>3</div> <div>2</div> <div>1</div> <div>0</div> <div>1</div>
Total number of measurements	448				

In the above description, the vertical and inclined axes c and a of Topsøe's description are interchanged. This was done to bring out a striking similarity between the primary prism zone of these monoclinic crystals of ammonium selenate and the primary prism zone of the rhombic crystals of ammonium sulphate, and the sulphates and selenates of potassium, rubidium, and caesium. In both cases there is close simulation to hexagonal symmetry. The angle $ap = (100):(110)$ of ammonium selenate is $59^\circ 38'$, $ap' = (100):(310)$ is $29^\circ 38'$, and $p'p = (310):(110)$ is $30^\circ 0'$; the corresponding angles in ammonium sulphate are $ap = (100):(110) = 29^\circ 24'$, and $pp' = (110):(130) = 30^\circ 0'$, together making $ap' = (100):(130) = 59^\circ 24'$. The angles in this zone are thus in both instances very nearly 30° and 60° , although the primary prism

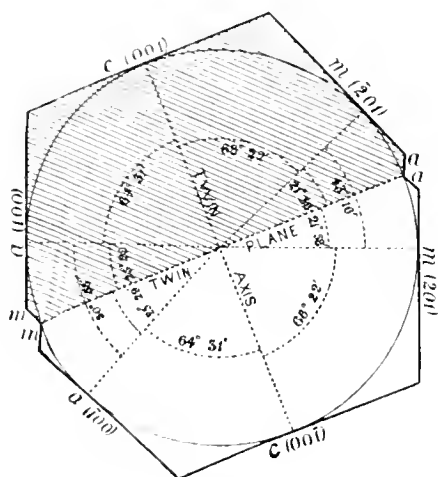


FIG. 6.

of the one appears to correspond most nearly to the tertiary prism of the other. Hence, while the basal plane is tilted in this (monoclinic) variety of ammonium selenate, the angles between the faces of the prism zone remain practically the same as in the rhombic variety. This order of setting up the crystals is thus adopted as being most probably the correct one as regards structure, and the topic axes have been calculated on the assumption of pseudo-hexagonal symmetry, exactly similar as regards the prism zone to that of the other sulphates and selenates of the alkali series.

Volume and Structure.

Relative Density.—The following six determinations were made by the suspension method, using a mixture of methylene iodide and

benzene as the immersion liquid. Small and very well-formed crystals grown in a vacuum were employed.

Temp. of observation.	Corresponding sp. gr. compared with water at 4°.	Calculated sp. gr. for 20°/4°.
18·4°	2·1937	2·1934
19·4	2·1945	2·1944
17·7	2·1938	2·1933
14·6	2·1952	2·1940
14·5	2·1951	2·1939
15·0	2·1942	2·1931
Mean		2·1937

The density of ammonium selenate, as crystallised in the ordinary monoclinic form, is therefore taken as 2·194 for 20°/4°.

The position of ammonium selenate in the selenate series as regards density will be seen from the following table to be similar to that of ammonium sulphate in the sulphate series, each being the lightest member of its series.

(NH ₄) ₂ SO ₄	1·772	(NH ₄) ₂ SeO ₄ ...	2·194
K ₂ SO ₄	2·666	K ₂ SeO ₄	3·067
Rb ₂ SO ₄	3·615	Rb ₂ SeO ₄	3·902
Cs ₂ SO ₄	4·246	Cs ₂ SeO ₄	4·456

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{177·98}{2·194} = 81·12. \quad \text{It will be seen from}$$

the following table of the molecular volumes of the eight salts of the series that the position of ammonium selenate is analogous to that of ammonium sulphate, namely, immediately following the rubidium salt.

K ₂ SO ₄	64·91	K ₂ SeO ₄	71·67
Rb ₂ SO ₄	73·34	Rb ₂ SeO ₄	79·94
(NH ₄) ₂ SO ₄ ...	74·04	(NH ₄) ₂ SeO ₄ ...	81·12
Cs ₂ SO ₄	84·58	Cs ₂ SeO ₄	91·09

Topic Axes.—These have been calculated both on the assumption of the ordinary monoclinic structure, and on that of pseudo-hexagonal structure, the latter for the reasons stated at the end of the last section. On the former assumption, χ , ψ , and ω represent the relative distances apart of the centres of gravity of the molecular structural units (Sohnke points) along the directions of the three monoclinic axes. They are given by the following formulæ, in which a , b , c are the axial ratios, and β is the angle between the inclined axes, a and c , while V is the molecular volume :

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \beta}}, \quad \psi = \sqrt[3]{\frac{V}{ac \sin \beta}}, \quad \omega = \sqrt[3]{\frac{c^2 V}{a \sin \beta}}.$$

Their values are : $\chi : \psi : \omega = 6.4456 : 3.4104 : 4.0880$.

On the latter (pseudo-hexagonal) assumption, the structural arrangement is as shown in Fig. 7, which represents a section through the crystal perpendicular to the primary prism zone $[apb]$. ψ represents the separation of the structural points along the symmetry axis b , and ω that along the vertical axis c ; but χ no longer represents the

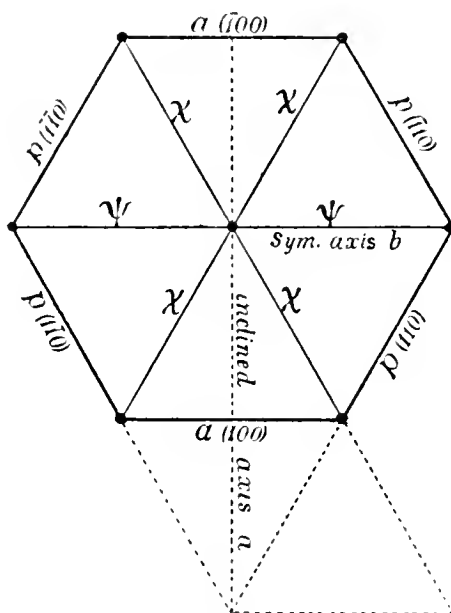


FIG. 7.

separation along the axis a , but along two pseudo-hexagonal axes, inclined to the plane of the paper, and whose plans lie at nearly 60° to each other and to the symmetry axis b (topic axis ψ). They are given by the following formulæ :

$$\chi = \frac{1}{2} \cdot \sqrt{1 + a^2} \cdot \sqrt[3]{\frac{2V}{ac \sin \beta}}, \quad \psi = \sqrt[3]{\frac{2V}{ac \sin \beta}}, \quad \omega = \sqrt[3]{\frac{2c^2 V}{a \sin \beta}};$$

and their numerical values are as under :

$$\chi : \psi : \omega = 4.5939 : 4.2968 : 5.1506.$$

It is interesting to compare these topic parameters of monoclinic ammonium selenate with those of the rhombic sulphates and selenates of the alkalis, as analogously pseudo-hexagonally expressed in the author's last communication (Trans., 1905, 87, 1188). On examining the table there given it will be observed that the topic parameters of

ammonium selenate are very similar to those in the table. The values of ψ and ω lie between those for potassium and caesium selenates, ψ being close to the caesium salt value and ω to the potassium salt value. The less strictly comparable pair of parameters χ are of the same order as the values of χ for the metallic selenates, being slightly greater than the value for caesium selenate. Although the individual parameters are naturally not so truly comparable as are

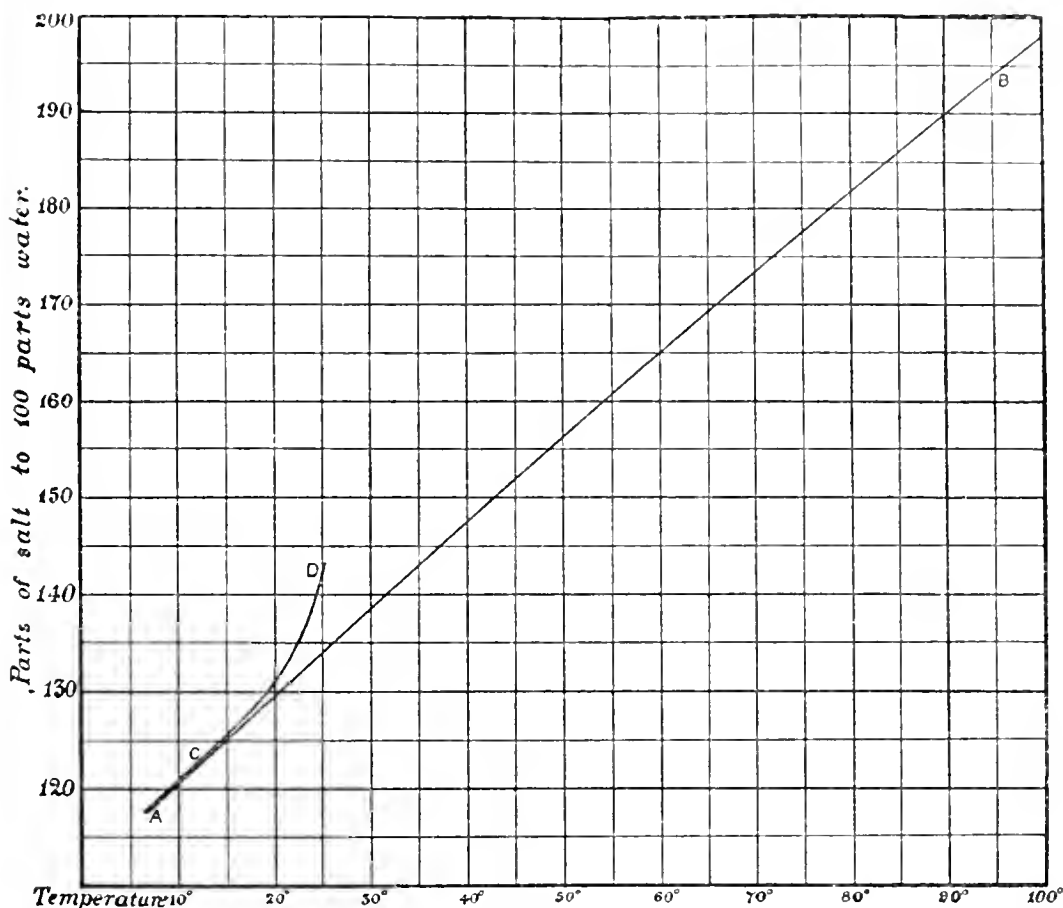


FIG. 8.

those of the rhombic salts among themselves, it is noteworthy that the average (mean of χ , ψ , and ω) of the parameters of ammonium selenate is intermediate between the averages for the rubidium and caesium salts.

Solubility.

Three determinations of the solubility of the monoclinic crystals of ammonium selenate were made, for saturation at 7°, 59°, and 100° respectively.

Determination of Solubility of Ammonium Selenate.

Weight of saturated solution taken.	Temp. of saturation.	Weight of anhydrous salt obtained.	Parts by weight of salt dissolved by 100 parts of water.
14.97 grams	7°	8.06 grams	117
26.01 "	59	16.17 "	164
16.46 "	100	10.91 "	197

It will be seen from the last column that water at the ordinary temperature dissolves slightly more than its own weight of ammonium selenate, and boiling water almost exactly twice its weight.

The results are graphically expressed in the longer curve (which is nearly a straight line), *AB*, in Fig. 8. The shorter curve, *CD*, is the super-solubility curve, which has been most kindly determined by Prof. Miers and Miss Isaac by the refraction method which they have recently described to the Society (Trans., 1906, 89, 413). It has been constructed from the following data which they have furnished :

Parts of salt to each 100 parts of water.	Maximum value of refractive index of solution reached.	Temperature at highest point.
142.5	1.42528	25°
130.22	1.42192	19.5
126.8	1.42127	16.2
124.35	1.42107	1

It will be observed that the supersolubility curve runs nearly parallel with, and very close to, the solubility curve at the lower temperatures in the neighbourhood of the ordinary, and that the two curves diverge from near 20° onwards at an accelerating rate. Hence at the ordinary temperature there is but a very narrow range of metastability between the unsaturated and the labile condition, while the range is considerably greater at a warm summer temperature.

On comparing this result with the results previously given for the metallic selenates (Trans., 1897, 71, 851), and for the same temperature of 12°, it will be seen that 100 parts by weight of water at 12° dissolve respectively 115 parts of potassium selenate, 122 parts of ammonium selenate, 159 parts of rubidium selenate, and 245 parts of caesium selenate. The solubility of ammonium selenate is thus only slightly greater than that of potassium selenate ; it is nearly twice as great as that of ammonium sulphate (74 parts in 100 of water).

Optics.

Orientation of Axes of Optical Ellipsoid.—Three determinations of the extinction directions in the symmetry plane were made with three section-plates ground parallel to the latter. One of the two extinction directions is very close to the normal to $c\{001\}$, as shown in Fig. 9, and the exact positions found for it are as under :

Section 1	1°49'	behind the normal to $c\{001\}$.
„ 2	2 9	„ „
„ 3	2 56	„ „
Mean ...		2°18'	

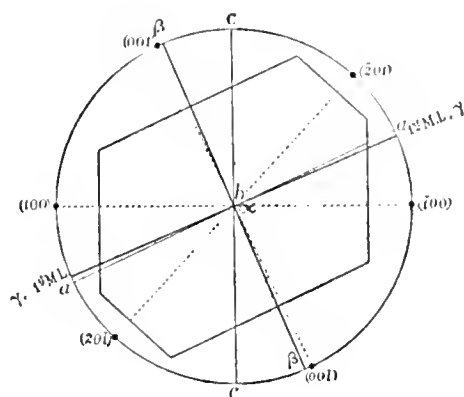


FIG. 9.

This direction in the symmetry plane is the intermediate axis β of the indicatrix or of the optical velocity ellipsoid, perpendicular to the plane containing the optic axes, which latter is thus perpendicular to the symmetry plane. The other direction of extinction (at 90° to the one measured) in the symmetry plane is the first median line and axis γ of the indicatrix or ϵ of the optical velocity ellipsoid. It is within half a degree of being midway between the normals to $a\{100\}$ and $m\{20\bar{1}\}$, being situated $23^\circ 11'$ from the former normal and $23^\circ 56'$ from the latter. The symmetry axis b is the second median line and axis a of the indicatrix or α of the velocity ellipsoid.

The sign of the double refraction is positive.

Refractive Indices.—These were determined with six 60° -prisms, each so ground as to give two indices directly. The results are given in the accompanying table.

Refractive Indices of Ammonium Selenate.

Index.	Nature of light.	Limits.	Mean.
α . Vibrations parallel to the symmetry axis (2 M.L.).	Li.....	1.5554—68	1.5561
	C.....	1.5565—79	1.5571
	Na.....	1.5598—613	1.5607
	Tl.....	1.5634—48	1.5641
	F.....	1.5681—90	1.5687
	G.....	1.5744—56	1.5752
β . Vibrations parallel di- rection in symmetry plane 2 18' behind the normal to c{001}.	Li.....	1.5576—88	1.5584
	C.....	1.5587—99	1.5594
	Na.....	1.5623—35	1.5630
	Tl.....	1.5659—70	1.5665
	F.....	1.5706—19	1.5713
	G.....	1.5775—83	1.5781
γ . Vibrations parallel to the first median line.	Li.....	1.5787—805	1.5796
	C.....	1.5797—815	1.5806
	Na.....	1.5839—55	1.5846
	Tl.....	1.5877—92	1.5885
	F.....	1.5929—42	1.5935
	G.....	1.6000—12	1.6005

Mean of α , β , and γ for Na-light, 1.5694.

The β index, corrected to a vacuum (correction = +0.0004) for light of any wave-length λ as far as that of the green thallium line, is represented absolutely by the following formula, which is also approximately valid for the blue end of the spectrum :

$$\beta = 1.5404 + \frac{988\ 153}{\lambda^2} - \frac{6\ 585\ 000\ 000\ 000}{\lambda^4} + \dots$$

The α indices are also very closely reproduced if the constant 1.5404 is diminished by 0.0024, and the γ indices if it is increased by 0.0216.

The *double refraction*, $\mu_{\gamma-\alpha}$, is as follows :

For Li-light	0.0235	For Tl-light	0.0244
„ C- „	0.0235	„ F- „	0.0248
„ Na- „	0.0239	„ G- „	0.0253

Refractive Indices at Higher Temperatures.—These were determined with two of the prisms, yielding respectively α and β , and β and γ . Determinations were made not only for 80°, as in the case of ammonium sulphate, but also for the temperature of 100°. For on heating the prism yielding α and β , the two images corresponding to these two indices, already unusually close together (separation 13' for Na-light), were observed to approach each other so that at 80° they were only 6' apart, overlapping at the broad ends of the images of the Websky slit and almost touching at the central narrow part. After the determination at 80°, the phenomena were followed further. At 87°, the images had approached to within 3', the central parts just touching. At 91°, their separation was further reduced to 2', at 96°

they were less than 1' apart, and at 100° they were identical for all wave-lengths. At this temperature, for which a series of determinations was carried out, the curious spectacle was observed of an apparently single image, which remained unextinguished for all positions of the nicol in front of the eyepiece. In reality, one image was being extinguished as fast as the other was coming into view, and thus their united intensity remained almost constant. It would have been quite so were it not for the fact that the image visible when the nicol is at 90° is always slightly fainter than that seen when the nicol is at 0°, owing to greater loss by reflection from the incident prism face. Beyond 100°, the images began to separate again on opposite sides of each other, so that α now became β and *vice versa*.

This condition of identity of two of the refractive indices, and thus of the temporary conversion of the optical ellipsoid into an ellipsoid of revolution, has been found by the author in previous cases, in which this series of salts has proved rich, to be accompanied by, and to be the explanation of, the phenomenon of crossed-axial-plane dispersion of the optic axes. It will subsequently be shown (p. 1093) that ammonium selenate is no exception to this rule.

Corresponding determinations at 80° and 100° were also made with the second prism affording β and γ , and the following table exhibits the combined results of both sets of determinations:

Nature of light.	Refractive indices for 80°.			Refractive indices for 100°.	
	α .	β .	γ .	α and β	γ .
Li	1.5556	1.5560	1.5761	1.5553	1.5757
C	1.5563	1.5568	1.5773	1.5561	1.5765
Na	1.5599	1.5605	1.5812	1.5593	1.5804
Tl	1.5637	1.5643	1.5852	1.5636	1.5843
F	1.5682	1.5689	1.5900	1.5682	1.5890

The images for G-light were not seen so well at these temperatures as at the ordinary temperature, owing to loss of light by reflection from the glass plates closing the heating apparatus.

Optic Axial Angle.—Three pairs of section-plates perpendicular to the first and second median lines were prepared with the aid of the cutting and grinding goniometer and afforded the following measurements, α -bromonaphthalene being the immersion liquid used for the determinations of 2*H* α and 2*H* σ .

Apparent Angle in Air, 2E.

Light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	58°20'	59°35'	59° 9'	59° 1'
C	58 53	59 43	59 30	59 22
Na	60 15	61 15	60 43	60 44
Tl	61 2	61 54	61 43	61 33
F	62 1	62 36	62 49	62 29

True Optic Axial Angle of Ammonium Selenate, 2Va.

Light.	No. of section perp. 1st M.L.	Observed values of 2Ha.	No. of section perp. 2nd M.L.	Observed values of 2Ho	Calculated values of 2Fa.	Mean value of 2Va.
Li	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 35^{\circ} 8' \\ 34 52 \\ 34 16 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 126^{\circ} 30' \\ 126 5 \\ 126 27 \end{array} \right.$	$\left\{ \begin{array}{l} 37^{\circ} 21' \\ 37 10 \\ 37 0 \end{array} \right.$	$\left. \right\} 37^{\circ} 10'$
C	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 35 13 \\ 35 1 \\ 34 55 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 126 20 \\ 125 52 \\ 126 17 \end{array} \right.$	$\left\{ \begin{array}{l} 37 28 \\ 37 20 \\ 37 10 \end{array} \right.$	$\left. \right\} 37 19$
Na	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 35 11 \\ 35 25 \\ 35 25 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 125 17 \\ 124 45 \\ 125 27 \end{array} \right.$	$\left\{ \begin{array}{l} 38 6 \\ 37 54 \\ 37 47 \end{array} \right.$	$\left. \right\} 37 54$
Tl.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 36 0 \\ 35 42 \\ 35 39 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 124 10 \\ 123 30 \\ 124 31 \end{array} \right.$	$\left\{ \begin{array}{l} 38 33 \\ 38 22 \\ 38 10 \end{array} \right.$	$\left. \right\} 38 22$
F	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 36 7 \\ 35 56 \\ 35 48 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 122 57 \\ 122 13 \\ 123 16 \end{array} \right.$	$\left\{ \begin{array}{l} 38 52 \\ 38 49 \\ 38 30 \end{array} \right.$	$\left. \right\} 38 44$

Horizontal Dispersion of the First Median Line.—As the first median line lies in the symmetry plane, whilst the second median line is identical with the symmetry axis, the former only is dispersed. The amount was determined by arranging the section-plate vertically instead of horizontally (the optic axes being separated in the longer direction of the plate, that of the elongated ortho-prism zone), and the nicols at 90° and 0° instead of at 45° and 135° . Each optic axis in turn was brought to the centre of the cross-wires by rotation of the back-to-front cylindrical adjusting movement of the polarising goniometer, and measurements were then made of the lateral difference of position of the axis for the usual six wave-lengths of light while the plate was immersed in (1) oil of cassia, and (2) oil of anise, whose refractive indices are just slightly higher and lower respectively than the mean index of ammonium selenate. Both series of determinations agreed in indicating that the first median line is dispersed, so that for blue light it is nearer to the normal to $a\{100\}$ than for red light. The amount is such that the two optic axes are $12'$ dispersed between C- and F-light, which corresponds to a dispersion of the first median line of $15'$.

Effect of Rise of Temperature on the Optic Axial Angle.—The refraction results had indicated the possibility of crossed-axial-plane dispersion at a temperature in the neighbourhood of 100° . Sections 1 and 2 were investigated with the aid of the heating apparatus of the larger Fuess' polarising goniometer and gave practically identical results, showing that the supposition was founded on fact.

The optic axes, separated by $59-62^\circ$ ($2E$) at the ordinary temperature, approached each other as the temperature rose. At 60° , the angle had become reduced to 45° for the middle of the spectrum, and at 75° to 40° . At 90° , the angle was only 30° , and at 100° it had become reduced to 23° . Still further heating caused the hyperbolic brushes to coalesce into the uniaxial rectangular cross, and the lemniscates and elliptic rings to become circles, for each wave-length in turn, beginning with the red, at successively higher temperatures, which are given in the following table, corrected for the conduction of the platinum crystal holder.

Corrected Temperatures for Formation of Uniaxial Cross.

For Li-light	110°
„ C „	111½°
„ Na „	114°
„ Tl „	116°
„ F „	119°

After forming the cross for each wave-length, the axes separated along the vertical diameter of the field, the second median line changing from the symmetry axis b to the third extinction direction nearly normal to $c\{001\}$, the plane of the optic axes thus changing into the symmetry plane.

It is remarkable that this is the fifth case of crossed-axial-plane dispersion in the simple and double series of alkali sulphates and selenates, the others being Rb_2SO_4 , Cs_2SeO_6 , $\text{Cs}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cs}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$. The cause, which would appear to be a general one as regards this phenomenon, has already been explained in the discussion of the refraction results.

Axes of the Optical Ellipsoids.

Axes of indicatrix.....	$a : \beta : \gamma = 0.9985 : 1 : 1.0138$
Axes of optical velocity ellipsoids ...	$a : b : c = 1.0015 : 1 : 0.9861$

Molecular Optical Constants.

Axis of optical indicatrix.	$a.$	$\beta.$	$\gamma.$
Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$	$\left\{ \begin{array}{l} C \ 0.1468 \\ G \ 0.1507 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1473 \\ 0.1514 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1519 \\ 0.1561 \end{array} \right.$
Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$	$\left\{ \begin{array}{l} C \ 26.13 \\ G \ 26.83 \end{array} \right.$	$\left\{ \begin{array}{l} 26.22 \\ 26.94 \end{array} \right.$	$\left\{ \begin{array}{l} 27.03 \\ 27.78 \end{array} \right.$
Specific dispersion, $n_G - n_C$	0.0039	0.0041	0.0042
Molecular dispersion, $m_G - m_C$	0.70	0.72	0.75
Molecular refraction, $\frac{n-1}{d} M$	$C \ 45.22$	45.41	47.13

Refraction in the State of Solution in Water.—Two determinations were made of the refraction equivalent in solution with solutions of two different degrees of concentration, the stronger of which was not far removed from saturation. The results are given in the next table; the molecular refractions are calculated for the ray C:

Molecular Refraction of Ammonium Selenate in Solution.

Weight of water.	Weight of salt.	Percentage of salt in solution.	Sp. gr. of solution at 20°/4°.	Refractive index of solution.	Molecular refraction of salt in dissolved state.
9.3513	8.7021	48.20	1.3627	$\left\{ \begin{array}{l} \text{Li} \dots\dots 1.4067 \\ \text{C} \dots\dots 1.4073 \\ \text{Na} \dots\dots 1.4098 \\ \text{Ti} \dots\dots 1.4122 \\ \text{F} \dots\dots 1.4151 \\ \text{G} \dots\dots 1.4198 \end{array} \right\}$	46.84
9.5981	7.5040	43.88	1.3248	$\left\{ \begin{array}{l} \text{Li} \dots\dots 1.3990 \\ \text{C} \dots\dots 1.3996 \\ \text{Na} \dots\dots 1.4020 \\ \text{Ti} \dots\dots 1.4043 \\ \text{F} \dots\dots 1.4073 \\ \text{G} \dots\dots 1.4114 \end{array} \right\}$	46.74
Mean refraction equivalent (Gladstone's) for the state of solution in water					46.79
" " " " " of the crystals (mean of all three values)					45.92
Difference.....					+0.87

Optical Comparison with other Salts of the Series.

Although the difference of system renders any comparison of the position of the respective optical ellipsoids invalid, it will be interesting to see how the refractive indices and the molecular optical constants of ammonium selenate compare with those of the other seven salts of the series.

It will at once be seen on comparing the table of refractive indices on p. 1090 with that previously given for the selenates of potassium, rubidium, and caesium (Trans., 1897, 71, 899) that the whole of the indices of ammonium selenate lie between those of rubidium and caesium selenates, and considerably closer on the whole to those of the rubidium salt. The best kind of comparison is given by placing side by side the mean values (mean of all three indices α , β , and γ) of the refractive index for the various salts, and this is done in the next table for the wave-length of sodium light.

Mean Refractive Indices.

K_2SO_4	1.4952	184	0.0144	K_2SeO_4	1.5396	149
Rb_2SO_4	1.5136	129	0.0109	Rb_2SeO_4	1.5545	149
$(\text{NH}_4)_2\text{SO}_4$	1.5256	379	0.0138	$(\text{NH}_4)_2\text{SeO}_4$	1.5694	303
Cs_2SO_4	1.5335		0.0362	Cs_2SeO_4	1.5997	

The position of the ammonium salt, just after the rubidium salt, is seen to be almost exactly the same in both sulphate and selenate series. Thus, the average refraction of monoclinic ammonium selenate is what would have been expected had the crystals been strictly isomorphous with those of the other members of the series. Also the difference between the mean refraction of ammonium sulphate and that of ammonium selenate, given in the central column, is of the same order as the difference between corresponding potassium or rubidium salts of the two series.

A similar fact will also be observed with respect to the relative dimensions of the optical ellipsoids if their axial ratios are relatively expressed, as in the next table, by taking the value for the potassium salt of each series along the axis b as unity. Although the directions of the ellipsoidal axes in the case of ammonium selenate are not strictly comparable with those of the others, the position of ammonium selenate is seen to be undoubtedly just after rubidium selenate, precisely as ammonium sulphate closely follows its analogue, rubidium sulphate.

Axial Ratios of Optical Velocity Ellipsoids.

K_2SO_4	0.9992 : 1	: 0.9975	K_2SeO_4	0.9975 : 1	: 0.9939
Rb_2SO_4	0.9862 : 0.9871	: 0.9869	Rb_2SeO_4 ...	0.9881 : 0.9895	: 0.9853
$(NH_4)_2SO_4$..	0.9742 : 0.9806	: 0.9820	$(NH_4)_2SeO_4$	0.9837 : 0.9822	: 0.9688
Cs_2SO_4	0.9536 : 0.9517	: 0.9575	Cs_2SeO_4	0.9593 : 0.9602	: 0.9596

Before any comparison of the optical constants could be made on absolutely analogous lines, it was considered desirable to recalculate the values of those constants for the four sulphates and the three selenates previously described, employing the new values of the densities, as determined by the suspension method, given in the paper presented last year on the topic parameters (Trans., 1905, 87, 1183). The values thus obtained will then be strictly comparable with those now published for ammonium selenate, and will also be nearer the truth than the values formerly given. They are set forth in the next tables.

$$\text{Specific Refraction, Lorenz, } \frac{n^2 - 1}{(n^2 + 2)d} = n.$$

	For ray U ($H\alpha$).			For ray near G ($H\gamma$).		
	$a.$	$b.$	$c.$	$a.$	$b.$	$c.$
$(NH_4)_2SO_4$...	0.1745	0.1718	0.1712	0.1784	0.1755	0.1749
K_2SO_4	0.1091	0.1088	0.1095	0.1108	0.1106	0.1111
Rb_2SO_4	0.0831	0.0829	0.0830	0.0846	0.0845	0.0845
Cs_2SO_4	0.0766	0.0764	0.0759	0.0782	0.0779	0.0771
$(NH_4)_2SeO_4$...	0.1473	0.1468	0.1519	0.1514	0.1507	0.1561
K_2SeO_4	0.1018	0.1012	0.1026	0.1042	0.1036	0.1051
Rb_2SeO_4	0.0818	0.0815	0.0824	0.0837	0.0835	0.0843
Cs_2SeO_4	0.0765	0.0763	0.0765	0.0784	0.0782	0.0783

Molecular Refraction, Lorenz, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m.$

	For ray C (<i>H</i> α).			For ray near <i>G</i> (<i>H</i> γ).		
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>a.</i>	<i>b.</i>	<i>c.</i>
K ₂ SO ₄	18·87	18·83	18·95	19·18	19·14	19·27
Rb ₂ SO ₄	22·04	21·99	22·00	22·44	22·39	22·40
(NH ₄) ₂ SO ₄	22·89	22·54	22·46	23·11	23·03	22·95
Cs ₂ SO ₄	27·51	27·44	27·26	28·07	27·99	27·79
K ₂ SeO ₄	22·37	22·24	22·56	22·91	22·77	23·11
Rb ₂ SeO ₄	25·52	25·43	25·71	26·12	26·04	26·30
(NH ₄) ₂ SeO ₄ ...	β26·22	α26·13	γ27·03	β26·94	α26·83	γ27·78
Cs ₂ SeO ₄	31·05	30·99	31·03	31·82	31·76	31·80
Specific dispersion, <i>n_G</i> - <i>n_C</i> .			Molecular dispersion, <i>m_G</i> - <i>m_C</i> .			
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>a.</i>	<i>b.</i>	<i>c.</i>
(NH ₄) ₂ SO ₄	0·0039	0·0037	0·0037	0·52	0·49	0·49
K ₂ SO ₄	0·0017	0·0018	0·0019	0·31	0·31	0·32
Rb ₂ SO ₄	0·0015	0·0016	0·0015	0·40	0·40	0·40
Cs ₂ SO ₄	0·0016	0·0015	0·0015	0·56	0·55	0·53
(NH ₄) ₂ SeO ₄ ...	β0·0041	α0·0039	γ0·0042	β0·72	α0·70	γ0·75
K ₂ SeO ₄ ...	0·0024	0·0024	0·0025	0·54	0·53	0·55
Rb ₂ SeO ₄	0·0019	0·0020	0·0019	0·60	0·61	0·59
Cs ₂ SeO ₄	0·0019	0·0019	0·0018	0·77	0·77	0·77

Molecular Refraction, Gladstone, $\frac{n - 1}{d} M$, for ray C (H α).

	a.	b.	c.	Mean.
K ₂ SO ₄	32·01	31·94	32·18	32·04
Rb ₂ SO ₄	37·61	37·52	37·53	37·55
(NH ₄) ₂ SO ₄	39·29	38·56	38·40	38·75
Cs ₂ SO ₄	47·71	47·56	47·17	47·48
K ₂ SeO ₄	38·46	38·19	38·86	38·50
Rb ₂ SeO ₄	44·00	43·82	44·36	44·06
(NH ₄) ₂ SeO ₄ ...	β 45·41	α 45·22	γ 47·13	45·92
Cs ₂ SeO ₄	54·41	54·28	54·37	54·35

Comparison of Refraction Equivalents for Crystalline and Dissolved States.

	Mean molecular refraction of crystals.	Molecular refraction in solution.		
		Separate determinations.	Mean.	Difference.
K ₂ SO ₄	32·04	{ 33·21 } 33·21	33·21	+1·17
Rb ₂ SO ₄	37·55	—	38·21	+0·66
(NH ₄) ₂ SO ₄	38·75	{ 39·30 } 39·51 39·47	39·43	+0·68
Cs ₂ SO ₄	47·48	—	47·27	−0·21
K ₂ SeO ₄	38·50	{ 39·55 } 39·71 39·69 39·65	39·65	+1·15
Rb ₂ SeO ₄	44·06	{ 44·72 } 44·53	44·63	+0·57
(NH ₄) ₂ SeO ₄ ...	45·92	{ 46·84 } 46·74	46·79	+0·87
Cs ₂ SeO ₄	54·35	{ 54·11 } 54·06	54·10	−0·25

The values for the densities, molecular weights, and molecular volumes of the seven salts other than ammonium selenate, which have been employed in the calculations, are those given in the topic axes memoir (*loc. cit.*, p. 1188).

The three specific and molecular refraction constants of ammonium selenate do not correspond as regards direction to the morphological axial directions a , b , c of the rhombic salts on account of the different (monoclinic) system of the crystals, the optical ellipsoid being rotated about the axis of symmetry b ; they are marked to show the axial direction of the indicatrix (ellipsoid), therefore, and whilst a is truly identical with the direction b , β and γ do not correspond to the morphological axial directions a and c , but to other rectangular directions in the same plane (the plane of symmetry).

The conclusions which have already been drawn in the author's previous memoirs as to the relations of the various salts with respect to their specific and molecular refraction and dispersion are all equally valid for these recalculated values.

The position of ammonium selenate in the selenate series will be observed throughout to be the same as that of ammonium sulphate in the sulphate series. As regards the most important property of molecular refraction, whether calculated by the formula of Lorenz or of Gladstone and Dale, this position is immediately after the rubidium salt. Thus, the fact that ammonium selenate crystallises with monoclinic symmetry, instead of rhombic like the rest of the series, does not appear to affect the specific and molecular optical constants, these being the same as would have been expected from a strictly isomorphous rhombic form. Such a rhombic form would doubtless have exhibited somewhat different directional values, but the average value would evidently have been near what is observed in the case of the monoclinic form. The mean values for the Gladstone molecular refraction are given in the table for those constants and will render this point clear.

A similar interesting resemblance of behaviour of ammonium selenate and ammonium sulphate is shown with respect to the difference between the values of the mean molecular refraction for the crystalline and dissolved states. In both cases, the difference is a positive one, less than that between the two states of the potassium salt and not far removed from that between the dissolved and crystalline rubidium salt, whereas the two states of the caesium salt in both series show a slight negative difference. The completion of the two series by the investigation of ammonium selenate now enables emphasis to be given to the statement already advanced in the metallic selenate memoir (*Trans.*, 1897, 71, 914), that Gladstone's generalisation that "the refraction equivalent of a solution is the sum

of the refraction equivalents of the solvent and of the substance dissolved" is substantially correct, slight differences due to change of state being on both sides of zero, and that the order of the differences follows the order of the atomic weights in the case of the alkali metals, whilst the ammonium salt takes up the position near the rubidium salt which has been shown to be its proper position in the series.

Summary of Results.

Normal ammonium selenate, $(\text{NH}_4)_2\text{SeO}_4$, crystallises differently from ammonium sulphate and the normal sulphates and selenates of potassium, rubidium, and caesium, the crystals possessing monoclinic symmetry, whereas the seven latter salts form a strictly related rhombic series, the characters and relationships of which have been described by the author in previous communications.

A rhombic form of ammonium selenate was once (in 1862) obtained by von Hauer and described by von Lang, and the historic specimen has been most kindly sent by Prof. von Lang from Vienna to the author. In spite of some deliquescence during the intervening forty-four years, ample confirmation of von Lang's results as to the system, principal angles, and optical character has been obtained. It has been found by specific gravity determinations by the suspension method that they are probably not quite pure, but contain admixed ammonium sulphate. Von Lang also mentioned a small quantity of acicular crystals of different optical character, and these turn out to be identical with the author's monoclinic form. These monoclinic needles are found to be purer than the rhombic crystals, in which, indeed, almost all the impurity (isomorphous) appears to have been concentrated.

Rhombic mixed crystals of ammonium selenate with ammonium sulphate, potassium selenate, and rubidium selenate respectively have been obtained, containing in the last case more than 60 per cent. of ammonium selenate. Monoclinic mixed crystals of ammonium selenate and sulphate have also been obtained containing 30 per cent. of the latter. It is therefore concluded that ammonium selenate is dimorphous and the whole series isodimorphous, and that the rhombic form which is not deposited from the pure solution under ordinary circumstances exists in mixed crystals. The presence of some admixed ammonium sulphate in von Hauer's solution of ammonium selenate is doubtless the explanation of the production of the rhombic crystals measured by von Lang.

The monoclinic crystals of ammonium selenate show a very similar pseudo-hexagonal primary prism zone (of almost exactly 60°) to that of the rhombic crystals of the other salts. Indeed, the monoclinic

crystals may be considered as being derived from the rhombic merely by the tilting of the basal plane from its rectangular to an inclined position with respect to the brachypinacoid. The crystals have been considered as arranged, for the purpose of description, analogously, so as to bring out this relationship, and the topic parameters have been calculated on the corresponding basis of a pseudo-hexagonal space lattice.

The topic parameters thus derived exhibit a close resemblance to those previously given for the seven rhombic members of the series, and their mean value is intermediate between the mean values for rubidium and cesium selenates.

The molecular volume, refractive indices, dimensions of the optical ellipsoid, and the molecular optical constants are singularly near what would have been expected had the crystals been truly isomorphically rhombic. With respect to all these constants, ammonium selenate takes its place in the series of selenates immediately after rubidium selenate, just as ammonium sulphate falls into place immediately after rubidium sulphate; indeed, this has now been shown by the author to be the general position of ammonium crystallographically in the alkali series.

As a side issue, a general explanation has been arrived at for the beautiful optical property of crossed-axial-plane dispersion of the optic axes, ammonium selenate forming the fifth case of this somewhat rare phenomenon which has been met with in the alkali series.

CX.—*The Constituents of the Essential Oil from the Fruit of Pittosporum undulatum.*

By FREDERICK BELDING POWER and FRANK TUTIN.

Pittosporum undulatum, Ventenat, is a tree indigenous to south-eastern Australia, where it is known to the English colonists by the popular names of "Native Laurel" and "Mock Orange" (compare *Select Extra-tropical Plants*, by Baron Ferd. von Mueller, 1884, p. 284, and *Pharmacographia Indica*, Vol. 1, p. 154).

In a communication to the Royal Society of N. S. Wales, on December 4th, 1895, Professor R. Threlfall, of the University of Sydney, described the general characters of the fruit of *Pittosporum undulatum*, and particularly noted that, when bruised, it develops a fragrant odour, resembling that of the tangerine orange, although easily distinguished from the latter. The flowers of this tree are also

known to possess an exquisite fragrance, which, however, is quite distinct from that of the fruit, and resembles that of orange blossoms.

In order to ascertain the nature of the odorous principle of *Pittosporum* fruit, Professor Threlfall subjected 50 kilograms of the entire fruit to steam distillation, and obtained therefrom about 180 c.c. of an essential oil. As the specific gravity of the latter was determined by him to be 0.848 at 24°, the yield of oil would correspond to about 0.3 per cent. of the weight of the fruit. He then submitted about 60 c.c. of the oil to a single fractional distillation, but none of these fractions were further examined, and they were subsequently sent to Professor W. A. Tilden, of the Royal College of Science, London, together with a small quantity of the original oil. Through the kindness of Professor Tilden, these specimens were placed at the disposal of one of us for further examination.

The oil distilled by Professor Threlfall was stated by him to have been dried by means of fused calcium chloride, and the portion received by us amounted to about 160 grams. After further drying with anhydrous sodium sulphate, and filtering, it was rectified by distillation. The rectified oil was pale yellow and had a pleasant odour, suggestive of the presence of a considerable proportion of limonene. Its density was 0.8638 at 15°, and its optical rotation +82°32' in a 1-dcm. tube. The oil was then subjected to a preliminary examination, but, as it had evidently undergone some change on keeping, we availed ourselves of the opportunity of having a larger quantity of the oil freshly distilled for us in Australia for the purpose of its more complete investigation.

Although Professor Threlfall in his paper (*loc. cit.*) has indicated that the *Pittosporum undulatum* is common in the bush around Sydney, this appears at present not to be the case, and a supply of fruit sufficient for the distillation of the oil could only be obtained from private gardens, where the tree is cultivated on account of the fragrance of the flowers. The distillation was conducted during the months of December and January, just before the period of ripening of the fruit, and while it was still green. From 220 kilograms of the fruit, 960 grams of essential oil were obtained, corresponding to a yield of 0.44 per cent.

EXPERIMENTAL.

The investigation here described was conducted entirely with the oil which had been freshly distilled for us in Australia, and the amount employed for this purpose was 900 grams. It is pale yellow, and has a pleasant odour resembling that of orange oil. After being dried with anhydrous sodium sulphate and filtered, it had a density of 0.8615 at 15°/15°, and an optical rotation of +74°4' in a 1-dcm. tube. It was insoluble in ten times its volume of 70 per cent. alcohol.

A determination of the amount of free acids and esters gave the following data: 20 grams of the oil required 0.2 c.c. of a semi-normal alcoholic solution of potassium hydroxide for the neutralisation of the free acids, and on subsequently adding an excess of alkali and boiling for thirty minutes, it was found that 4 c.c. of semi-normal alkali were required for the hydrolysis of the esters present.

The entire oil was then shaken several times successively with small portions of 20 per cent. sulphuric acid, and afterwards washed well with water. The acid aqueous liquid was freed from adhering oil by shaking with ether, then made alkaline with potassium hydroxide, and again shaken with ether. After washing the ethereal liquid and drying it by means of potassium carbonate, the ether was removed, but only a trace of brown, resinous matter was obtained, thus indicating the absence of any basic substance such as methyl anthranilate.

About 20 c.c. of the oil were shaken for four hours with a saturated solution of sodium bisulphite, but it yielded no solid compound, nor did the aqueous bisulphite liquid contain any aldehyde or ketone.

As the amount of free acids contained in the oil was so very small, it was, after treatment with the dilute sulphuric acid, directly extracted several times successively with a 5 per cent. solution of potassium hydroxide, and subsequently washed with water. The alkaline aqueous liquid, after being freed from adhering oil, was acidified with sulphuric acid and extracted with ether, the ethereal solution being subsequently shaken with a solution of sodium carbonate to remove any acids, and finally washed with water. On removing the ether, a very small brown residue was obtained, which had an odour resembling that of eugenol and gave a brown colour with ferric chloride, but no definite benzoyl derivative could be prepared from it.

The sodium carbonate liquid, which contained the acids from the preceding extraction with potassium hydroxide, was acidified with sulphuric acid and extracted with ether. On removing the ether, a very small quantity of a brown oil was obtained, which had a strong odour of valeric acid and gave an intense violet coloration with ferric chloride. This violet coloration was apparently due to the presence of a trace of salicylic acid. The oily liquid, after standing some time, deposited crystals which, after several crystallisations from alcohol, melted at 62° , and evidently consisted of palmitic acid, since the melting point was not changed on mixing the substance with an equal amount of pure palmitic acid.

Preliminary Examination of the Terpenes.

As a preliminary test for the presence of an olefinic or other unstable terpene, the oil, which had previously been treated with dilute sulphuric

acid and with alkali, as above described, was dried with anhydrous sodium sulphate, and then distilled under 60 mm. pressure. The portion which boiled below 110° was collected, and, after submitting this to several fractionations under a pressure of 20 mm., the density of a fraction boiling below 70° was determined, and found to be 0.8466 at $15^{\circ}/15^{\circ}$, which proved the absence of any olefinic terpene. These liquids were then distilled under the ordinary pressure, and the following fractions collected: below 165° ; $165-170^{\circ}$; $170-172^{\circ}$. The density of the fraction $165-170^{\circ}$ was found to be 0.8471 at $15^{\circ}/15^{\circ}$, thus confirming the absence of myrcene. The fraction $170-172^{\circ}$ was specially tested for phellandrene, but with a negative result.

Hydrolysis of the Oil.

All the oil boiling above 190° under the ordinary pressure was hydrolysed by boiling with an alcoholic solution of 7 grams of potassium hydroxide for about half an hour in a flask provided with a reflux condenser. After being allowed to cool, water was added, and the separated oil collected, washed, and dried with anhydrous sodium sulphate. It was then distilled under 60 mm. pressure, which removed a small amount of non-volatile, resinous matter.

Fractional Distillation of the Oil.

The hydrolysed oil, together with the portion which had previously been separated under diminished pressure, was then submitted to repeated distillation under the ordinary pressure, when the following fractions were ultimately obtained: below 165° ; $165-169^{\circ}$; $169-173^{\circ}$; $173-180^{\circ}$; $180-185^{\circ}$; $185-195^{\circ}$; $195-205^{\circ}$; $205-215^{\circ}$; $215-225^{\circ}$; $225-235^{\circ}$; $235-245^{\circ}$; $245-255^{\circ}$; $255-270^{\circ}$; $270^{\circ}+$. The last-mentioned fraction was a viscid, green oil, and amounted to only 3.8 grams.

Identification of Pinene.

Fraction below 165° .—This was a colourless, limpid liquid, which commenced to boil at about 157° and had an odour of pinene. It was nearly insoluble in 70 per cent. alcohol, and amounted to 23 grams.

0.1077 gave 0.3444 CO_2 and 0.1141 H_2O . C = 87.2; H = 11.8.

$\text{C}_{10}\text{H}_{16}$ requires C = 88.2; H = 11.8 per cent.

$d_{15^{\circ}/15^{\circ}} = 0.8515$; $n_D + 61^{\circ}50'$ in a 1-dm. tube.

This fraction evidently consisted of a hydrocarbon, and was found to contain pinene, as it yielded a small amount of a crystalline nitrosochloride, from which the corresponding nitrobenzylamine, melting at

123°, was prepared. The fraction was also examined for camphene, but with a negative result.

Fraction 165—169°.—The weight of this fraction was 18 grams.

0.1324 gave 0.4274 CO₂ and 0.1401 H₂O. C = 88.0; H = 11.8.

$d_{15}^{15}/15^{\circ} = 0.8494$; $\alpha_D + 73^{\circ}50'$ in a 1-dm. tube.

Fraction 169—173°.—The weight of this fraction was 27 grams.

0.1352 gave 0.4345 CO₂ and 0.1428 H₂O. C = 87.6; H = 11.7.

$d_{15}^{15}/15^{\circ} = 0.8482$; $\alpha_D + 79^{\circ}36'$ in a 1-dm. tube.

Both this fraction and that immediately preceding it were colourless, limpid liquids, and evidently consisted of a mixture of pinene with the constituent of the following fraction.

Identification of Limonene.

Fraction 173—180°.—This fraction represented by far the largest portion of the oil, and amounted to 485 grams. It was a colourless, highly refractive liquid, having the characteristic odour of limonene, and on analysis was found to consist entirely of a hydrocarbon.

0.1140 gave 0.3679 CO₂ and 0.1214 H₂O. C = 88.0; H = 11.8.

C₁₀H₁₆ requires C = 88.2; H = 11.8 per cent.

$d_{15}^{15}/15^{\circ} = 0.8488$; $\alpha_D + 89^{\circ}10'$ in a 1-dm. tube.

It was readily identified as *d*-limonene by the formation of the tetrabromide, which, after recrystallisation from ethyl acetate, melted at 104°.

Fraction 180—185°.—The weight of this fraction was 46 grams.

0.1161 gave 0.3657 CO₂ and 0.1211 H₂O. C = 85.9; H = 11.6.

$d_{15}^{15}/15^{\circ} = 0.8588$; $\alpha_D + 82^{\circ}42'$ in a 1-dm. tube.

This fraction evidently also consisted to a large extent of *d*-limonene.

Fraction 185—195°.—The weight of this fraction was only 4.8 grams.

0.1083 gave 0.3347 CO₂ and 0.1128 H₂O. C = 84.3; H = 11.6.

$d_{15}^{15}/15^{\circ} = 0.8727$; $\alpha_D + 66^{\circ}48'$ in a 1-dm. tube.

It was evidently a mixture of the hydrocarbon contained in the preceding fractions with the oxygenated substance contained in the succeeding ones.

Fraction 195—205°.—This fraction, which was very pale yellow, amounted to only 4.1 grams.

0.1251 gave 0.3736 CO₂ and 0.1293 H₂O. C = 81.4; H = 11.5.

$d_{15}^{15}/15^{\circ} = 0.8938$; $\alpha_D + 46^{\circ}32'$ in a 1-dm. tube.

It was specially tested for linalool, but with a negative result.

Fraction 205—215°.—The weight of this fraction was 5.9 grams. It was light yellow, and possessed a pleasant, somewhat camphoraceous and rose-like odour.

0.1287 gave 0.3720 CO_2 and 0.1328 H_2O . $\text{C} = 78.8$; $\text{H} = 11.5$.

$d_{15}^{15} = 0.9179$; $n_D^{20} + 27.8'$ in a 1-dm. tube.

As this fraction was very small, it was further examined in connection with the following one.

Fraction 215—225°.—This fraction resembled the immediately preceding one in odour, and amounted to 8.2 grams.

0.1018 gave 0.2964 CO_2 and 0.1057 H_2O . $\text{C} = 79.4$; $\text{H} = 11.5$.

$d_{15}^{15} = 0.9242$; $n_D^{17} + 17.0'$ in a 1-dm. tube.

This fraction and the preceding one evidently contained the greater proportion of the oxygenated constituent of the oil, and as their total weights amounted to only 14 grams, they were mixed together for the purpose of further examination.

A portion of the mixed liquid was treated with semicarbazide, but no semicarbazone could be obtained from it. The remainder of the liquid was therefore carefully oxidised by adding it slowly to a mixture of eight times its weight of potassium bichromate and twelve times its weight of sulphuric acid, the latter having been previously diluted with three times its volume of water. After the first action had ceased, the mixture was gently heated on a water-bath, with frequent shaking, for half an hour, then cooled, and repeatedly extracted with ether, which removed a yellow, oily substance. The latter was subjected to steam distillation, when nearly all passed over. The non-volatile portion was examined for the oxidation products of terpineol, but with a negative result. The oil contained in the distillate, which had a somewhat coumarin-like odour, was extracted with ether, the ethereal liquid freed from a trace of acid by shaking with a solution of sodium carbonate, washed, dried, and the ether removed. The oil thus obtained was treated in methyl alcohol solution with semicarbazide hydrochloride and sodium acetate, and allowed to stand overnight. On the addition of water, a rather viscid oil was precipitated, which did not become crystalline, and steam was therefore passed through the mixture in order to remove any uncombined oil, after which the semicarbazone solidified on cooling. It was accompanied by a considerable amount of gummy matter, but, after being dried and then recrystallised several times from alcohol, it was obtained in tufts of small needles, which melted at 174° . It was analysed with the following result:

0.0775 gave 0.1739 CO_2 and 0.0591 H_2O . $\text{C} = 61.2$; $\text{H} = 8.5$.

$\text{C}_{10}\text{H}_{17}\text{ON}_3$ requires $\text{C} = 61.5$; $\text{H} = 8.7$ per cent.

On warming a small quantity of this semicarbazone with dilute sulphuric acid, the regenerated substance was observed to possess a strong coumarin-like odour.

From the analytical figures it would appear that the semicarbazone is derived from a ketone (or aldehyde) having the formula $\text{C}_9\text{H}_{14}\text{O}$, and as no substance reacting with semicarbazide was originally present in the fractions oxidised, it is probable that these contained an alcohol of the formula $\text{C}_9\text{H}_{16}\text{O}$. This view is also in accordance with the low percentage of hydrogen found in the respective fractions, for $\text{C}_9\text{H}_{16}\text{O}$ requires $\text{H} = 11.4$ per cent., whereas an alcohol of the formula $\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{H} = 11.7$ per cent.

The semicarbazone described above does not appear to be identical with any heretofore obtained, but as the amount of substance was so very small, it was not possible to pursue its investigation further.

Fraction 225—235°.—The weight of this fraction was 5.2 grams. It was pale yellow and had a distinctly rose-like odour.

0.1323 gave 0.3907 CO_2 and 0.1361 H_2O . $\text{C} = 80.5$; $\text{H} = 11.4$.

$d_{15^\circ/15^\circ} = 0.9236$; $n_D + 11^\circ 56'$ in a 1-dm. tube.

The properties of this fraction indicated that it might contain some geraniol or a similar alcohol of rose-like odour. An attempt was therefore made to prepare the corresponding diphenylurethane, and also to isolate the alcohol by means of its conversion into the acid phthalic ester, but the amount of material was so exceedingly small that we were unable definitely to identify any constituent of it.

Fraction 235—245°.—The amount of this fraction was only 2.7 grams.

0.1087 gave 0.3287 CO_2 and 0.1130 H_2O . $\text{C} = 82.5$; $\text{H} = 11.6$.

$d_{15^\circ/15^\circ} = 0.9238$; $n_D + 6^\circ 32'$ in a 1-dm. tube.

Fraction 245—255°.—The weight of this fraction was 5.3 grams.

0.1183 gave 0.3757 CO_2 and 0.1239 H_2O . $\text{C} = 86.6$; $\text{H} = 11.6$.

$d_{15^\circ/15^\circ} = 0.9138$; $n_D + 0^\circ 56'$ in a 1-dm. tube.

This fraction and that immediately preceding it also possessed a rose-like odour, and they evidently consisted of a mixture of some of the oxygenated constituent of a preceding fraction with the constituent of the following one.

Isolation of a New Sesquiterpene.

Fraction 255—270°.—This was a relatively large fraction, amounting to 83.2 grams. It was a yellow, slightly viscous liquid, having a decidedly fragrant odour. It was almost insoluble in 70 per cent. alcohol.

0.1205 gave 0.3855 CO_2 and 0.1264 H_2O . $\text{C} = 87.2$; $\text{H} = 11.7$.

$d_{15^\circ/15^\circ} = 0.9169$; $n_D + 0.8'$ in a 1-dem. tube.

The analysis and physical constants of this fraction indicated that it consisted of a nearly pure, optically inactive sesquiterpene. It distilled almost entirely between 260° and 265° , and for the most part between 263° and 264° . For its further purification it was twice distilled over metallic sodium under 60 mm. pressure, when it almost entirely passed over between 167° and 171° .

The substance thus obtained was a slightly viscid liquid, having a pale straw colour and a delicate rose-like fragrance. It was again analysed and its constants determined with the following result.

0.1210 gave 0.3896 CO_2 and 0.1276 H_2O . $\text{C} = 87.8$; $\text{H} = 11.7$.

$\text{C}_{15}\text{H}_{24}$ requires $\text{C} = 88.2$; $\text{H} = 11.8$ per cent.

$d_{15^\circ/15^\circ} = 0.9100$; optically inactive; $n_D^{20^\circ} = 1.5030$.

Molecular refraction 66.22.

When to a solution of a drop of the sesquiterpene in 5 c.c. of glacial acetic acid a drop of concentrated sulphuric acid is added, a purplish-red coloration is produced, which gradually increases in intensity.

No solid nitrosate or nitrosite could be obtained from this sesquiterpene. The attempts to prepare a nitrosochloride, both by Tilden's method, as employed by Chapman in the case of humulene (Trans., 1895, 67, 61), and the method adopted by Schreiner and Kremers (*Pharm. Arch.*, 1899, 2, 293) were equally unsuccessful. On treatment with bromine in chloroform it yielded an intensely violet-coloured liquid, but this evolved much hydrogen bromide, and no solid compound could be obtained from it. The hydrochloride was prepared by saturating an ethereal solution of the sesquiterpene with dry hydrogen chloride at -5° , and allowing it to stand for twenty four hours, but on removing the solvent a brown, heavy oil was obtained, which could not be crystallised even when cooled to -15° .

Although it was impossible to obtain any solid derivative of this sesquiterpene, and thereby definitely characterise it, it is evident that it is not identical with either of the two previously known

optically inactive sesquiterpenes, as will be seen from the following comparison of their properties :

	Humulene.	Limene.	Sesquiterpene from Pittosporum oil.
Boiling point (ordinary pressure)	263—266 (corr.)	262—263° (uncorr.)	263—264° (corr.)
Density, 15° (15°)	0.9001	0.873	0.9100
Refractive index, n_D^{20}	1.5021	1.4910	1.5030
Hydrochloride	Liquid	Crystals, m. p. 79—80°	Liquid.
Nitrosochloride	M. p. 164—165°	“Unsatisfactory”	Could not be obtained.
Nitrosite	„ 120—121	„	„
Nitrosate	„ 162—163	—	„

The sesquiterpene obtained from the essential oil of the fruit of *Pittosporum undulatum* may thus be regarded as a compound which has not hitherto been described. Its molecular refraction indicates that it belongs to the group of dicyclic sesquiterpenes with two ethylenic linkings, which also includes humulene (Trans., 1895, 67, 60, 780), whereas the other known optically inactive sesquiterpene, limene, evidently belongs to the group of monocyclic compounds with three ethylenic linkings (Trans., 1904, 85, 416; Ber., 1906, 39, 657).

Acids obtained by the Hydrolysis of the Oil.

The strongly alkaline aqueous liquid which was separated from the hydrolysed oil, as previously described, was freed from adhering oil by shaking with ether. It was then acidified with sulphuric acid and again extracted with ether, the ethereal liquid well washed with water, dried, and the ether removed. A brown, oily liquid was thus obtained, which possessed a strong odour of valeric acid, and amounted to about 2 grams. The acids contained in this liquid were converted into the potassium salts, from which, by the addition of silver nitrate, the corresponding silver salts were precipitated in eight fractions. These were washed, dried in a vacuum over sulphuric acid, and analysed :

Fraction	I.	0.1570 of silver salt gave 0.0700 Ag.	Ag = 44.58.
„	II.	0.2372 „ „ „ 0.1170 Ag.	Ag = 49.32.
„	III.	0.2210 „ „ „ 0.1132 Ag.	Ag = 51.22.
„	IV.	0.2073 „ „ „ 0.1064 Ag.	Ag = 51.33.
„	V.	0.1746 „ „ „ 0.0900 Ag.	Ag = 51.54.
„	VI.	0.1112 „ „ „ 0.0577 Ag.	Ag = 51.89.
„	VII.	0.1435 „ „ „ 0.0748 Ag.	Ag = 52.13.
„	VIII.	0.1173 „ „ „ 0.0615 Ag.	Ag = 52.43.

$C_5H_9O_2Ag$ requires Ag = 51.67 per cent.

It is evident, therefore, that these acids consisted for the most part of valeric acid, together with very small amounts of acids of a lower and higher molecular weight.

The aqueous liquid, from which these acids had been removed by means of ether, contained a very small amount of formic acid.

Summary.

The results of this investigation have shown that the essential oil of *Pittosporum undulatum* contains the following substances :

d-Pinene, about 4 per cent.

d-Limonene, about 75 per cent.

Esters of valeric, formic, and other acids, a small amount.

An optically inactive *sesquiterpene*, about 15 per cent.

Palmitic acid and an undetermined phenol, in very small amount, and apparently a trace of salicylic acid.

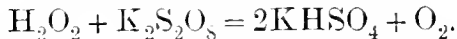
In conclusion, the authors desire to express their thanks to Professor W. A. Tilden for having brought this oil under their notice, and for kindly placing at their disposal the specimen of it in his possession.

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CXI.—*A Study of the Reaction between Hydrogen Peroxide and Potassium Persulphate.*

By JOHN ALBERT NEWTON FRIEND, M.Sc.

WHEN aqueous solutions of hydrogen peroxide and potassium persulphate are mixed, bubbles of gas are set free, and the mixture becomes acid to litmus. This at once suggests the reaction



But accurate estimations of hydrogen peroxide cannot be obtained by direct titration with potassium permanganate in the presence of potassium persulphate (Friend, *Trans.*, 1904, **85**, 597 ; compare Inglis, *Trans.*, 1903, **83**, 1014). Hence, it was not until a suitable method for its estimation under these conditions had been devised (Friend, *Trans.*, 1905, **87**, 1367) that a detailed investigation of this reaction became possible.

In what follows, *N*/50 permanganate was used, being made fresh each

day by dissolving 0.632 gram of the crystals in cold water and diluting to one litre. The thiosulphate was $N/100$ which had been made several days previously (Dupré, *Zeit. angew. Chem.*, 1904, 17, 815). The potassium persulphate was recrystallised and free from sulphate, and the hydrogen peroxide was from Merck, and guaranteed to be pure. The reactions were conducted in a thermostat, at 25° , in "Resistance" flasks which were well steamed out before use.

It was first necessary to determine whether equivalent quantities of peroxide and persulphate disappeared during the reaction. Neutral solutions of these were therefore mixed, and at regular intervals two portions of 2 c.c. each were removed as quickly as possible. One portion was poured into from 8 to 12 c.c. of about $7N$ sulphuric acid, a slight excess of permanganate rapidly added, and the excess estimated iodometrically according to the instructions given in a previous paper (Trans., 1905, 87, 1367). This gave the amount of peroxide. The remaining 2 c.c. were poured into a known volume of acidified ferrous sulphate solution which was then heated to the boiling point and the excess of ferrous sulphate estimated with permanganate. This gave the total oxidising power of the solution due to the peroxide and persulphate (Le Blanc and Eckardt, *Zeit. Elektrochem.*, 1899, 5, 355). Subtraction gave the amount of the latter. Owing to the slowness of the reaction, the error caused by the short interval of time which elapsed between successive withdrawals of the 2 c.c. was negligible.

The results are given in series I and II, where A and B represent the initial concentrations of the peroxide and persulphate respectively, calculated in c.c. of $N/50$ permanganate, whilst x_1 and x_2 represent the amount of decomposition of the same after any time t .

Series I.

Time in minutes.	$A - x_1$.	x_1 .	$B - x_2$.	x_2 .
0	15.88 c.c.	—	15.31 c.c.	—
90	14.88 „	1.00	14.22 „	1.09
150	13.69 „	2.19	13.12 „	2.19
300	11.00 „	4.88	10.34 „	4.97
Two days	1.01 „	14.87	0.34 „	14.97

Series II.

Time in minutes.	$A - x_1$.	x_1 .	$B - x_2$.	x_2 .
0	27.20 c.c.	—	7.20 c.c.	—
45	26.64 „	0.56	6.69 „	0.51
85	26.12 „	1.08	6.15 „	1.05
240	24.79 „	2.41	4.80 „	2.40
320	24.16 „	3.04	4.24 „	2.96

It was found in every case that $x_1 = x_2$. Hence, for every molecule of peroxide which disappeared, a molecule of persulphate also dis-

appeared, even when, as in series II, the concentration of the former was much greater than that of the latter.

This shows that the equation given above represents, at any rate, the initial and final stages of the reaction.

The Velocity of the Reaction.

In order to discover if the reaction took place in stages, it was now necessary to determine its rate. Solutions containing equivalent quantities of peroxide and persulphate were mixed, the velocity of decomposition of the former alone being measured. The results of one such experiment are given in series III, where k_1 and k_2 are calculated according to the formulæ for uni- and bi-molecular reactions respectively. In order to avoid the disturbing effects of the period of induction (*vide infra*) on the values of the constants, the first titration was neglected, that made one hour after mixing being taken as the initial titration, and its time as 0.

Series III.

Time in hours.	$A - x.$	$x.$	$k_1.$	$A \times k_2.$
0	14.78 c.c.	—	—	—
1	14.06 „	0.72 c.c.	0.0217	0.0512
2	13.19 „	1.59 „	0.0247	0.0603
3.5.....	12.05 „	2.73 „	0.0253	0.0647
4.5.....	11.35 „	3.43 „	0.0255	0.0672
6	10.36 „	4.42 „	0.0257	0.0711
8	9.16 „	5.62 „	0.0259	0.0767

It will be seen that the values for k_2 show no approach to constancy. The reaction, therefore, is unimolecular. But this conclusion could not be so readily drawn from all the reactions. It occasionally happened that there was but little to choose between the values for k_1 and k_2 . But it is important to notice that whilst the majority of the reactions were found (as in series III) to yield constant values for k_1 , and variable for k_2 , no cases were encountered in which the converse was true.

The dilution formulæ of van't Hoff and Noyes could not be used to verify this, for they gave contradictory results. This was because no two reactions at different dilutions were strictly comparable (compare Donnan and Le Rossignol, *Trans.*, 1903, **83**, 709). For example, on one occasion a reaction was begun with $A = B = 13.25$ c.c. At the expiration of twenty-two hours, the amount decomposed was 9.04 c.c., whilst a few days previously, when $A = B = 16.80$ c.c., the concentration had only fallen by 7.35 c.c. in the same number of hours. At other times the exact opposite would occur. Price and Denning (*loc. cit.*) have called attention to similar behaviour in the presence of colloidal

platinum. This cannot be due to the catalytic action of the decomposition products of glass, since it is shown later that the sulphates of sodium, potassium, and manganese exert only a slight action on the mixtures even in concentrated solutions. It is more probably caused by a variation in the length of the period of induction (*vide infra*) consequent upon the changes in dilution.

The fact that the reaction is unimolecular and not bimolecular, as we should expect from the equation, may be explained on the assumption that an intermediate compound is first formed between the peroxide and persulphate, and this, being more unstable than either, rapidly decomposes. It is the rate of decomposition of this compound which is measured. This is in agreement with the theory advanced by Kastle and Loevenhart (*Amer. Chem. J.*, 1903, 29, 563) and is supported by the two following facts:

(1) Since a molecule of peroxide disappears for every molecule of persulphate, the rate of decomposition of the one indicates that of the other. The results given in series IV and V indicate that the velocity of decomposition of the persulphate is independent of the concentration of the peroxide, always provided that the latter is present in excess.

Series IV.

$A = 26.14$ c.c. ; $B = 8.06$ c.c.

Time in hours.	$A - x$.	x .
0	26.14 c.c.	—
4	23.80 „	2.34 c.c.
8	22.12 „	4.02 „
15	20.34 „	5.80 „
21	19.54 „	6.60 „

Series V.

$A = 18.75$ c.c. ; $B = 8.06$ c.c.

$A - x$.	x .
18.75 c.c.	—
16.86 „	2.09 c.c.
15.28 „	3.67 „
13.37 „	5.58 „
12.53 „	6.42 „

This result is precisely what we should expect. If with a certain concentration of peroxide the main part of the persulphate is combined to form an intermediate product, a further addition of the former would not appreciably alter the amount of this compound, and hence its rate of decomposition would remain unaltered.

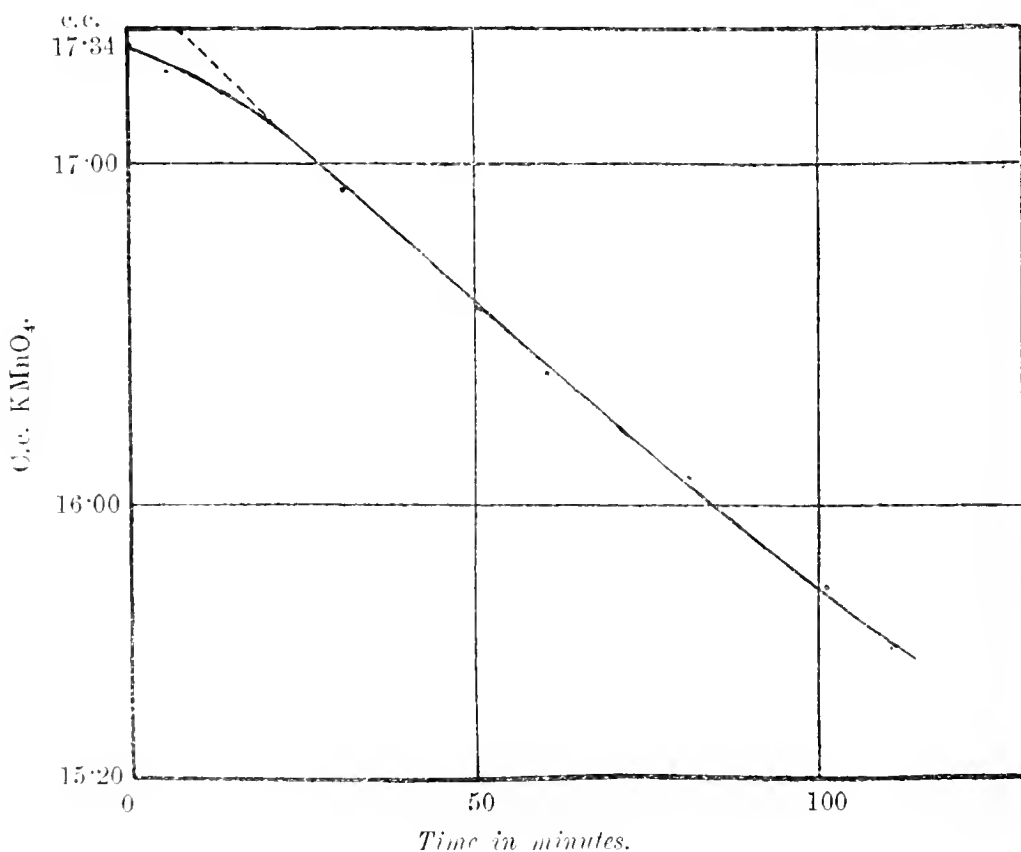
Too much reliance, however, must not be placed on this kind of evidence, since it has been pointed out that experiments performed at different dilutions are not always strictly comparable.

(2) When curves for the reactions were drawn, a "period of induction" was found to exist. This affords very strong evidence in favour of the theory of the formation of an intermediate compound, for the delay occasioned by its formation is a necessary consequence of the law of mass action (compare Mellor, *Trans.*, 1902, 81, 1280). In some cases, the period of induction appears to consist of two parts: (i) a period of inactivity during which no chemical action takes place, and

(ii) a period of gradually increasing chemical activity. In order to discover whether these two periods could be distinguished in the present case, a series of experiments was carried out in which the concentration of the peroxide was determined every few minutes. Series VI is a typical experiment, and the results are given in the curve.

Series VI.— $A = B$.

Time in minutes.	$A - x$.	Time in minutes.	$A - x$.	Time in minutes.	$A - x$.
0	17.34 c.c.	31	16.90 c.c.	81	16.08 c.c.
6	17.26 „	41	16.75 „	101	15.62 „
13	17.21 „	51	16.57 „	111	15.47 „
21	17.11 „	61	16.37 „	—	—

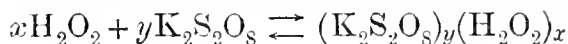


It will be seen that no period of inactivity is apparent.

Isolation of Intermediate Compound.

Compounds of hydrogen peroxide and various salts have been isolated (see Mellor, *Chemical Statics and Dynamics*, 1904, p. 331, where a full list of references is given). It was thought, therefore, that it might be possible to effect a separation of the compound between hydrogen peroxide and potassium persulphate, of whose existence we

have already had several indications. Most of the compounds which have hitherto been prepared have consisted of the peroxide attached to a stable salt; for example, cadmium chloride, as in $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}_2$ (Staedel, 1902), or ammonium sulphate, as in $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$ (Willstätter, 1903), but in the present case we are dealing with a persulphate which is unstable in solution, and which is readily attacked by the peroxide. It was therefore to be expected that the compound would be excessively unstable, and difficult to isolate. Solutions of hydrogen peroxide and potassium persulphate were mixed at -10° in a vessel surrounded by ice and salt. The half-frozen mass remained neutral to litmus for upwards of fifteen minutes, showing that at this low temperature the velocity of the reaction was very small. No indication, however, could be obtained of the formation of an additive compound. Some powdered persulphate was then put in a glass basin, covered with concentrated peroxide, and placed in a desiccator over sulphuric acid. Bubbles of oxygen gas were rapidly evolved, together with a trace of ozone, whose presence could be detected (i) by a faint odour, (ii) by its action on a filter paper soaked in an alcoholic solution of 4:4'-tetramethyldiaminodiphenylmethane (Arnold and Menzel, *Ber.*, 1902, 35, 1324; Fischer and Braehmer, *Ber.*, 1906, 39, 943; Arnold, *ibid.*, 1528). In the course of a few weeks, the peroxide had evaporated and a white, crystalline mass remained. A portion of this was dissolved in very dilute sulphuric acid, evolving bubbles of gas and emitting a faint crackling sound. The presence of hydrogen peroxide was indicated by the titanium sulphate test. As this might have been due to negative crystals of peroxide, the remainder was finely powdered and left in the desiccator. Some days later, the powder was removed and found to dissolve in dilute sulphuric acid, evolving bubbles of gas and leaving peroxide in solution, as before. The powder was kept for several weeks and tested from time to time. Gradually, however, the hydrogen peroxide disappeared. It is highly probable, therefore, that in this way the intermediate compound had been isolated in an impure form, and that on contact with water it decomposed into oxygen, potassium sulphate and persulphate, and hydrogen peroxide, the reaction



being reversible.

A few experiments were made in order to determine the relative amounts of the two constituents, but inconclusive results were obtained owing to the impossibility of preparing the pure substance.

If in the above formula $x = y = 1$, the compound, $\text{K}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}_2$, has the same empirical formula as the potassium salt of Caro's permonosulphuric acid. But no indications were ever obtained of the

formation of the latter salt, which has been recently prepared and described by Price (Trans., 1906, 89, 53).

The Influence of Sulphuric Acid.

As shown in series VII, VIII, and IX, sulphuric acid greatly retards the reaction provided it is present in sufficient amount to decompose all the persulphate. If less than this quantity is present, its effect is scarcely perceptible. This is in accordance with previous results (Trans., 1904, 85, 601; 1905, 87, 1369; compare Baubigny, *Compt. rend.*, 1903, 136, 449, 1325), and is probably due to the liberation of persulphuric acid, which is but slightly dissociated, thus hindering the formation of the intermediate compound.

Series VII.

$$A = B. \quad m \propto \text{H}_2\text{SO}_4.$$

Series VIII.

$$A = B. \quad m/3.5 \text{ H}_2\text{SO}_4.$$

Series IX.

$$A = B. \quad m/1.8 \text{ H}_2\text{SO}_4.$$

Time in

hours.	$A - x.$	$x.$	$A - x.$	$x.$	$A - x.$	$x.$
0	14.07 c.c.	—	14.07 c.c.	—	14.07 c.c.	—
2	12.12 „	1.95	13.07 „	1.00	13.18 „	0.89
5.5	8.99 „	5.08	10.99 „	3.08	11.62 „	2.45

It was interesting to determine if equivalent quantities of peroxide and persulphate disappeared in acid as well as in neutral solution. With this object, series X and XI were performed in an exactly similar manner to series I and II.

Series X.— $m/6 \text{ H}_2\text{SO}_4$.

Time in hours.	$A - x_1.$	$x_1.$	$B - x_2.$	$x_2.$
0	15.41 c.c.	—	16.41 c.c.	—
2	13.87 „	1.54	15.01 „	1.40
4.5	12.15 „	3.26	13.35 „	3.06
21	4.93 „	10.48	6.52 „	9.89

Series XI.— $m/6 \text{ H}_2\text{SO}_4$.

Time in hours.	$A - x_1.$	$x_1.$	$B - x_2.$	$x_2.$
0	21.15 c.c.	—	15.48 c.c.	—
3	19.94 „	1.21	14.25 „	1.23
7	18.12 „	3.03	12.74 „	2.74
23.5	13.34 „	7.81	8.11 „	7.37

The peroxide shows a slight tendency to disappear more rapidly than the persulphate. In addition to the main reaction, the side reaction



also takes place.

The Effect of Colloidal Platinum.

This has already been studied by Price and Denning (*loc. cit.*), but as these authors estimated the peroxide in the presence of persulphate by direct titration with permanganate, their results required verification.

The colloidal platinum was prepared, according to the method given by Bredig (*Zeit. physikal. Chem.*, 1899, **31**, 258), by Messrs. Philip Harris & Co. (Birmingham), to whom I am glad to have this opportunity of expressing my indebtedness. The concentration of the solution was not determined, this being deemed unnecessary.

Series XII and XIII show how closely two series of experiments agree when performed at the same time and with solutions of similar concentration; but comparable results could not be obtained when the concentrations were varied. In order to avoid the disturbing effects of the period of induction, the platinum was added after the peroxide and persulphate had been mixed for fifteen minutes.

Series XII and XIII.—A = B.

Time in minutes.	$A - x.$	$x.$	$A - x.$	$x.$
1	14.11 c.c.	—	13.95 c.c.	—
6	11.24 „	2.87	11.68 „	2.27
11	10.21 „	3.90	10.05 „	3.90
16	9.01 „	5.10	8.73 „	5.22
20	8.04 „	6.07	7.76 „	6.19
26	6.80 „	7.31	6.49 „	7.46

In series XIV and XV are given the results of estimating both components in neutral and acid solution respectively. They were performed in an exactly similar manner to series I and II, but, owing to the increased velocity of the reaction, it was necessary to allow for the interval of time elapsing between the successive withdrawals of 2 c.c. from the reaction mixture.

Series XIV.— m/∞ H_2SO_4 .

Time in minutes.	$A - x_1.$	$x_1.$	$B - x_2.$	$x_2.$
1.5.....	16.40 c.c.	—	15.42 c.c.	—
30.5	13.32 „	3.08	14.84 „	0.58
80.5.....	11.07 „	5.33	13.82 „	1.60
150.5	8.89 „	7.51	12.29 „	3.13
220.5.....	7.22 „	9.18	11.33 „	4.09

Series XV.— $m/6$ H_2SO_4 .

Time in minutes.	$A - x_1.$	$x_1.$	$B - x_2.$	$x_2.$
1.5.....	12.35 c.c.	—	12.52 c.c.	—
16.5.....	11.08 „	1.27	12.30 „	0.22
31.5.....	10.41 „	1.94	12.36 „	0.16
46.5	9.91 „	2.44	12.08 „	0.44
66.5.....	9.34 „	3.01	12.05 „	0.47

In neutral solution, the peroxide decomposed rather more than twice as rapidly as the persulphate, whilst in acid solution the latter scarcely underwent any decomposition at all. This result agrees with that obtained by Price and Denning (*loc. cit.*, p. 94).

The Effect of Dissolved Sulphates.

It was thought that the study of the effect of soluble sulphates on the reaction might throw further light on the retarding action of sulphuric acid.

1. *Sodium Sulphate*.—The pure anhydrous salt (Kahlbaum) was used. In concentrated solutions it exerted a slight, but decided, retarding action, probably caused by a suppression of the dissociation of the persulphate, owing to the presence of so many neutral ions.

Time in hours.	$m/\infty \text{ Na}_2\text{SO}_4$ $A - x.$	$m/10 \text{ Na}_2\text{SO}_4$ $A - x.$	$m/5 \text{ Na}_2\text{SO}_4$ $A - x.$
0	15.50 c.c.	15.50 c.c.	15.50 c.c.
7	10.36 „	10.96 „	11.04 „
20	5.46 „	6.59 „	6.80 „
47	1.96 „	2.65 „	2.85 „

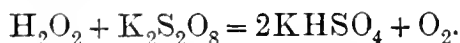
2. *Manganese Sulphate*.—The salt on analysis was found to be free from iron, and to be correctly represented by the formula $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. We might expect this salt to accelerate the reaction, for manganese dioxide is gradually precipitated from solutions containing manganese sulphate and potassium persulphate, and is immediately dissolved again on addition of hydrogen peroxide. It was found, however, that even $m/10$ solutions exerted a very slight retarding action on the initial stages of the reaction. This shows that it is not the Mn^{++} ion which renders inaccurate the direct titration of hydrogen peroxide with potassium permanganate in the presence of persulphates (compare Inglis, *loc. cit.*). As the reaction proceeded towards completion, however, a slight accelerating action was observed.

3. *Potassium Sulphate*.—The pure anhydrous salt (Kahlbaum) was used, and was found to exert a retarding action very similar to that of sodium sulphate.

Summary.

The results given in this paper may be briefly summarised as follows :

1. Solutions of hydrogen peroxide and potassium persulphate interact according to the equation :



2. The reaction is unimolecular, due to the formation of a highly unstable intermediate compound.

3. This compound may be prepared in an impure form by evaporating a mixture of hydrogen peroxide and potassium persulphate over sulphuric acid.

4. Sulphuric acid has a retarding effect on the reaction, as have the sulphates of sodium, potassium and manganese—the last named accelerating slightly as the reaction nears completion.

5. Colloidal platinum accelerates the reaction, the hydrogen peroxide undergoing rapid additional decomposition.

In conclusion, I have pleasure in thanking the Research Fund Committee for a grant which has defrayed the greater part of the expense entailed by this work.

THE GRAMMAR SCHOOL,
WATFORD.

CXII.—*Optically Active Reduced Naphthoic Acids.* *Part II. The Resolution of the Tetrahydronaphthoic Acids.*

By ROBERT HOWSON PICKARD and JOSEPH YATES.

THE tetrahydronaphthoic acids were prepared by von Baeyer and his co-workers (*Annalen*, 1891, 266, 198) by the reduction of the naphthoic acids by means of sodium in boiling amyl alcohol. Each contains an asymmetric carbon atom. We have therefore resolved them into their optical antipodes by the fractional crystallisation of the *l*-menthylamine salts in order to compare the molecular rotatory power of each with that of the Δ^2 (or Δ^3)-dihydro-1-naphthoic acid (Part I, *Trans.*, 1905, 87, 1766). The readiness with which these resolutions can be carried out affords another example of the usefulness of *l*-menthylamine for the resolution of inactive acids (compare Pickard and Neville, Part I, *loc. cit.*, and Neville, this vol., 384).

The active ion of 1:2:3:4-tetrahydro-1-naphthoic acid has a molecular rotatory power which is very much less than that of the corresponding Δ^2 -dihydro-acid. This is doubtless due to the proximity of the double linking to the asymmetric carbon atom.

The results obtained are compared in the following table :

Molecular rotatory power.	<i>l</i> -1:2:3:4-Tetrahydro-1-naphthoic acid.	<i>l</i> -1:2:3:4-Tetrahydro-2-naphthoic acid.	Δ^2 (or Δ^3)-Dihydro-1-naphthoic acid.
Acid in CHCl_3	- 28.1°	- 91.2°	$\pm 370.4^\circ$
Acid in C_6H_6	- 92.1	- 87.9	± 309.5
Sodium salt in H_2O ..	- 21.1	- 90.5	± 374.5

Resolution of 1 : 2 : 3 : 4-Tetrahydro-1-naphthoic Acid.

l-Menthylamine 1-1 : 2 : 3 : 4-Tetrahydro-1-naphthoate.—The racemic acid (1 mol.) was dissolved in the calculated quantity of sodium bicarbonate solution and mixed with a solution of *l*-menthylamine hydrochloride (1 mol.). The pasty mass of the l-B-l-A and l-B-d-A salts, which is immediately precipitated, soon becomes hard and brittle. It then melts indefinitely at below 100°, and has $[\alpha]_D$ about -18.5° in absolute alcohol. The products from four successive crystallisations of this from acetone had $[\alpha]_D$ in absolute alcohol -20.6° , -26.0° , -28.9° , -29.3° . The pure l-B-l-A salt was obtained from the fifth recrystallisation in large, glassy, stout prisms melting at 123°.

0.3710 made up to 19.8 c.c. with absolute alcohol gave $\alpha - 1.10^\circ$; * whence $[\alpha]_D - 29.35^\circ$ and $[M]_D - 97.1^\circ$.

The salt was boiled with a known excess of sodium hydroxide until all the menthylamine was driven off, when the hydroxide remaining was titrated.

0.5654 treated in this way used 0.0656 NaOH. The calculated quantity required is 0.0683 NaOH.

1-1 : 2 : 3 : 4-Tetrahydro-1-naphthoic Acid.—The pure l-B-l-A salt was treated with an excess of sodium carbonate and the menthylamine removed by ether. The *l*-acid, obtained from the aqueous solution of the sodium salt by precipitation with hydrochloric acid, crystallises from light petroleum in colourless, glistening plates melting at 52.5°. The purity of the acid was proved by combustion and titration experiments.

The following polarimetric observations were made :

0.3259 made up to 20 c.c. with chloroform gave $\alpha - 0.52^\circ$; whence $[\alpha]_D - 15.95^\circ$ and $[M]_D - 28.07^\circ$.

0.3480 made up to 19.8 c.c. with benzene gave $\alpha - 1.84^\circ$; whence $[\alpha]_D - 52.34^\circ$ and $[M]_D - 92.12^\circ$.

0.2812 exactly neutralised by 19.8 c.c. of a solution of NaOH gave $\alpha - 0.34^\circ$; whence the sodium salt has $[\alpha]_D - 10.64^\circ$ and $[M]_D - 21.07^\circ$.

The *mercurous*, *lead*, *silver*, and *ferric* salts are insoluble, whilst the *mercuric*, *zinc*, *manganese*, *magnesium*, *calcium*, and *barium* salts are soluble in water.

l-Menthylamine d-1 : 2 : 3 : 4-tetrahydro-1-naphthoate was obtained from the most soluble fractions in the acetone mother liquors. It

* All polarimetric observations recorded in this paper were made in a 2-dm. tube.

crystallised in hard, rhombic crusts, melted not very sharply at 78° , and had $[\alpha]_D - 12.79^{\circ}$ in absolute alcohol.

The *dextro*-acid obtained from this salt was not quite pure. When crystallised from light petroleum, it melted at $49-50^{\circ}$ and had $[\alpha]_D + 14.01^{\circ}$ in chloroform. A mixture of equal parts of this acid and the pure *levo*-isomeride was crystallised once from light petroleum, when it melted at 82° and was obtained in the characteristic crystalline form of the racemic acid, which melts at 85° (Baeyer, *loc. cit.*).

Resolution of 1 : 2 : 3 : 4-Tetrahydro-2-naphthoic Acid.

The resolution of the corresponding tetrahydro-2-naphthoic acid was carried out in a similar manner with *l*-menthylamine. The mixture of 1-B-1-A and 1-B-d-A salts had $[\alpha]_D - 22.86^{\circ}$ in absolute alcohol. The pure 1-B-1-A salt was obtained after ten crystallisations from acetone in the form of stout, rhombic prisms which melted at 150° .

0.3027 made up to 20 c.c. with absolute alcohol gave $\alpha - 1.67^{\circ}$; whence $[\alpha]_D - 55.17^{\circ}$ and $[M]_D - 182.6^{\circ}$.

The salt was analysed as before:

0.5283 used 0.0660 NaOH. The calculated quantity required is 0.0639 NaOH.

1-1 : 2 : 3 : 4-Tetrahydro-2-naphthoic acid crystallises in prismatic needles from light petroleum and melts at 99° , that is, 3° higher than the inactive acid (Baeyer, *loc. cit.*).

0.2798 made up to 20 c.c. with chloroform gave $\alpha - 1.45^{\circ}$; whence $[\alpha]_D - 51.82^{\circ}$ and $[M]_D - 91.2^{\circ}$.

0.2764 made up to 20 c.c. with benzene gave $\alpha - 1.38^{\circ}$; whence $[\alpha]_D - 49.96^{\circ}$ and $[M]_D - 87.9^{\circ}$.

The sodium salt is precipitated as a microcrystalline powder when ether is added to its solution in alcohol.

0.2315 gave 0.0761 Na_2SO_4 . $\text{Na} = 10.65$.

0.3094 lost 0.0257 when heated at 105° . $\text{H}_2\text{O} = 8.30$.

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{NaH}_2\text{O}$ requires $\text{Na} = 10.65$; $\text{H}_2\text{O} = 8.33$ per cent.

0.2746 made up to 20 c.c. with water gave $\alpha - 1.15^{\circ}$; whence $[\alpha]_D - 41.88^{\circ}$ and $[M]_D - 90.5^{\circ}$.

The *silver*, *lead*, *mercurous*, *mercuric*, *copper*, *ferric*, *zinc*, and *cadmium* salts are insoluble, whilst the *manganese*, *magnesium*, *barium*, and *calcium* salts are soluble in water.

d-1 : 2 : 3 : 4-Tetrahydro-2-naphthoic Acid.—The pure 1-B-d-A salt is very soluble in acetone and was not obtained pure, the purest specimen

having $[\alpha]_D + 1.66^\circ$ in absolute alcohol. The acid prepared from this salt crystallised from dilute acetic acid in stout, prismatic needles and melted at 99° .

0.3073 made up to 20 c.c. with chloroform gave $\alpha + 1.24^\circ$; whence $[\alpha]_D + 40.35^\circ$.

0.2986 made up to 19.9 c.c. with benzene gave $\alpha + 1.08^\circ$; whence $[\alpha]_D + 35.98^\circ$.

The difference exhibited in the rotation of 1:2:3:4-tetrahydro-1-naphthoic acid when dissolved in benzene and in chloroform is probably due to association with the solvent in the case of the benzene. This assumption is supported by the following ebullioscopic determinations of the molecular weights, for which we are indebted to Mr. Tom Thornley.

	Solvent.	Concentration of solution. Per cent.	Apparent molecular weight.
<i>r</i> -1:2:3:4-Tetrahydro-1-naphthoic acid.....	CHCl_3	2.5	176
" " "	C_6H_6	2.1	349
" " "	C_6H_6	4.7	296
<i>l</i> -1:2:3:4-Tetrahydro-1-naphthoic acid.....	C_6H_6	3.9	312
<i>d</i> -1:2:3:4-Tetrahydro-2-naphthoic acid.....	C_6H_6	2.3	234
" " "	CHCl_3	1.7	213

We wish to express our thanks to the Research Fund Committee of the Society for a grant which has defrayed some of the cost of the material for this work.

MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

CXIII.—*The Constitution of Umbellulone.*

By FRANK TUTIN.

IN the course of a chemical examination of the essential oil of Californian Laurel (*Umbellularia Californica*), Power and Lees (Trans., 1904, 85, 629) isolated a new ketone, which they designated "umbellulone." This ketone was shown to have the formula $\text{C}_{10}\text{H}_{14}\text{O}$, and to contain only one ethylenic linking, which indicated the presence of two closed rings. Power and Lees also showed that umbellulone behaves abnormally when treated with semicarbazide or hydroxylamine, for not only does the usual reaction with the carbonyl group take place on treatment with either of these reagents, but a molecule of the base also becomes attached to the carbon atoms of the

ethylenic linking. This behaviour has been shown by Harries and his pupils (*Ber.*, 1897, **30**, 230), by Tiemann (*Ber.*, 1897, **30**, 251, and 1900, **33**, 562), and by Rupe and Schlechoff (*Ber.*, 1903, **36**, 4377) to be a property of those ketones which contain an ethylenic linking in the $\alpha\beta$ -position with respect to the carbonyl group. It was therefore indicated that umbellulone was an $\alpha\beta$ -unsaturated cyclic ketone containing two closed rings.

The behaviour of umbellulone towards certain reagents was further studied by Lees (*Trans.*, 1904, **85**, 639), and the results obtained by him may be summarised as follows:

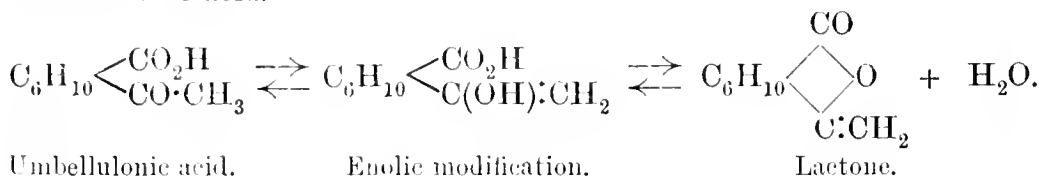
On treatment with bromine, umbellulone formed a liquid dibromide, which, on distillation under diminished pressure, gave solid dibromodihydroumbellulone, $C_{10}H_{14}OBr_2$, an unsaturated liquid monobromoumbellulone, $C_{10}H_{13}OBr$, and a small amount of a hydrocarbon, $C_{10}H_{14}$. The unsaturated monobromoumbellulone, on reduction with zinc dust and acetic acid, yielded a saturated ketone, $C_{10}H_{16}O$, whilst on submitting dibromodihydroumbellulone to a similar treatment monobromodihydroumbellulone, $C_{10}H_{15}OBr$, was obtained; the latter, on reduction with sodium in alcohol, gave tetrahydroumbellulol, $C_{10}H_{20}O$. It was also stated that "umbellulone is readily oxidised by potassium permanganate, yielding a lactone, $C_9H_{12}O_2$, together with several acids which were not further investigated."

As Mr. Lees has been unable to continue the investigation of this ketone, the author, in agreement with him, has further studied the derivatives of umbellulone, more especially the products of its oxidation with potassium permanganate. The present communication embodies the results obtained, and the conclusions which may be drawn from them respecting the constitution of this ketone.

Throughout this investigation it has been borne in mind that the material available for the greater part of the work could not be regarded as a pure substance, as it represented a fraction of the essential oil collected over a range of 10 degrees. Control experiments were therefore made with the use of pure umbellulone which had been regenerated from its semicarbazido-semicarbazone, and the compounds here described as derivatives of umbellulone are only such as were obtained from the pure ketone.

When umbellulone, $C_{10}H_{14}O$, is oxidised with cold permanganate, a *monocarboxylic keto-acid*, $C_9H_{14}O_3$ (b. p. 193—195°/50 mm.; m. p. 102°), is the principal product. This has been designated *umbellulonic acid*. It yields a crystalline oxime (m. p. 169—170°), and evidently contains the group $-CO\cdot CH_3$, since, on warming with iodine in presence of sodium carbonate, it readily gives iodoform. The umbellulonic acid thus obtained is associated with smaller amounts of acids of higher boiling point, but these could not be isolated in a state of purity owing

to the presence of oxidation products derived from substances other than umbellulone contained in the fraction of oil employed. When this mixture of acids is slowly distilled under 20 mm. pressure, water is eliminated, and a portion of the umbellulonic acid passes into an *unsaturated lactone*, $C_9H_{12}O_2$ (b. p. 129—135°/50 mm.), which, on solution in potash, again yields the keto-acid. This lactone is, in fact, produced by the elimination of water from the enolic modification of umbellulonic acid.

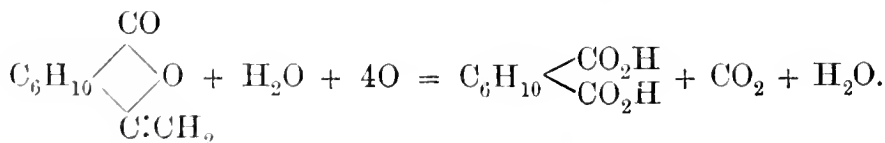


The change from keto-acid to lactone also takes place, but to a less extent, when pure umbellulonic acid is distilled under diminished pressure. The explanation of the phenomenon, that a larger proportion of umbellulonic acid becomes converted into lactone on distilling the crude mixture of acids than when the pure acid alone is distilled, probably lies in the fact that the acids associated with the umbellulonic acid in the former case are of higher boiling point, and also give rise to anhydrides* which assist in the abstraction of water and formation of the lactone. This supposition receives support from the fact that umbellulonic acid was found to pass into the lactone on boiling with acetic anhydride.

This unusual change from keto-acid into unsaturated lactone, and *vice versa*, is accompanied by a remarkable change in optical rotation, as the former has $[\alpha]_D + 377.6^\circ$ and the latter $[\alpha]_D - 210.58^\circ$.

From the formation of umbellulonic acid, $C_6H_{10}(\text{CO}_2\text{H})\text{CO} \cdot \text{CH}_3$, by the oxidation of umbellulone, $C_{10}H_{14}O$, it would appear that the latter contains the complex $C_6H_{10} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CMe} \end{array} \text{CH}$.

The lactone, when shaken into an emulsion with water, is readily oxidised by potassium permanganate, giving a quantitative yield of a polymethylene dicarboxylic acid, $C_8H_{12}O_4$ (m. p. 120—121°; $[\alpha]_D - 89.7^\circ$), for which the name *umbellularic acid* is proposed.



Umbellularic acid passes into the anhydride (b. p. 167—169°/50 mm.) when heated to about 150°, and is remarkably stable, for all further

* Umbellularic acid is probably present.

attempts to break down the molecule resulted in failure. It was therefore impossible to obtain more direct evidence regarding the constitution of umbellularic acid, but the following considerations afford indirect evidence, which may be considered fairly conclusive.

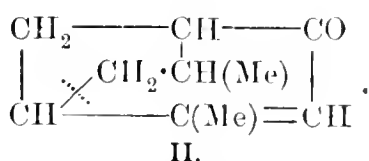
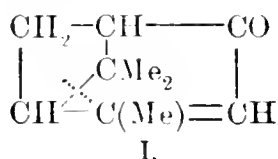
The general properties, and especially the great stability, of umbellularic acid indicate that it is one of the tetra-, penta-, or hexamethylene dicarboxylic acids. The latter consideration may be at once dismissed, as the four possible hexamethylene dicarboxylic acids are all known, and umbellularic acid does not agree in melting point with any of them. Of the methylpentamethylene dicarboxylic acids, only the 1-methyl-3:3-dicarboxylic acid is known, and of the dimethyltetramethylene* dicarboxylic acids only norpic acid, the 2:2-dimethyl-1:3-dicarboxylic acid, is known, with neither of which is umbellularic acid identical.

By the bromination of umbellulone and subsequent distillation of the product, Lees obtained, in addition to products containing bromine, a small amount of a hydrocarbon, $C_{10}H_{14}$, but expressed the opinion that this compound was derived from some substance other than umbellulone contained in the oil employed. This hydrocarbon has now been obtained from pure umbellulone, and has been identified as *p*-cymene.

Although the formation of *p*-cymene from umbellulone cannot very well be traced by any cycle of direct chemical changes, it would appear probable that the molecule of umbellulone contains a carbon skeleton which is capable of yielding a compound having methyl and isopropyl groups in the para-position without undergoing any profound structural change.

Any structural formula which would represent the constitution of umbellulone must, therefore, fulfil the following conditions. In the first place, it must contain a dimethyltetramethylene or a methylpentamethylene ring. United to this ring there must be the group $-CO \cdot CH : CMe-$, and, lastly, it must have a carbon framework capable of yielding, in a simple manner, paramethyl and isopropyl groups.

The only formulæ which are capable of fulfilling these conditions are the following :



Both of these compounds would yield paramethyl and isopropyl groups through the rupture of the diagonal bridge by the addition of

* The possibility of the occurrence of an ethyl group need not be considered, as this group does not occur among natural terpene derivatives and allied compounds.

hydrogen at the place indicated by the dotted line. A ketone of formula (I) contains a dimethyltetramethylene ring, and, on oxidation, would yield a norpic acid; whilst one of formula (II) contains a methylpentamethylene ring and would give 1-methylpentamethylene 3 : 5-dicarboxylic acid.

Umbellularic acid is, therefore, either a stereoisomeride of norpic acid or of 1-methylpentamethylene 3 : 5-dicarboxylic acid.

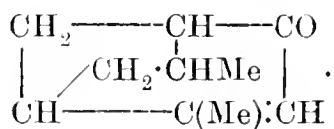
Norpic acid gives no anhydride and is apparently the *trans*-modification of inactive 2 : 2-dimethyltetramethylene 1 : 3-dicarboxylic acid. Umbellularic acid readily yields an anhydride, therefore it apparently represents a *cis*-modification, and it has not been found possible either to racemise it or to convert it into the corresponding *trans*-acid. It was therefore impossible directly to decide whether umbellularic acid is *l-cis*-norpic acid, but for the following reasons it appears extremely improbable. In the first place, if umbellularic acid is *l-cis*-norpic acid, then umbellulonic acid is *d*-pinononic acid, and this compound would not differ in boiling point from the inactive pinononic acid obtained by Wagner by the oxidation of pinene; whereas the methyl ester of Wagner's acid boils at 130—135°/14 mm. (*Ber.*, 1896, **29**, 881), and the ethyl ester of umbellulonic acid at about 130° under 20 mm. pressure.

In addition to this, if umbellulone is a keto-pinene (formula I), it would be expected that the norpic acid derived from it would become racemised, just as inactive norpic acid is obtained from active pinene; whereas umbellularic acid is not only optically active, but it has been found impossible to racemise it.

It would therefore appear probable that umbellularic acid is not *l-cis*-norpic acid, but *l*-1-methylpentamethylene 3 : 5-dicarboxylic acid, and that its persistent optical activity is due to the stable asymmetric

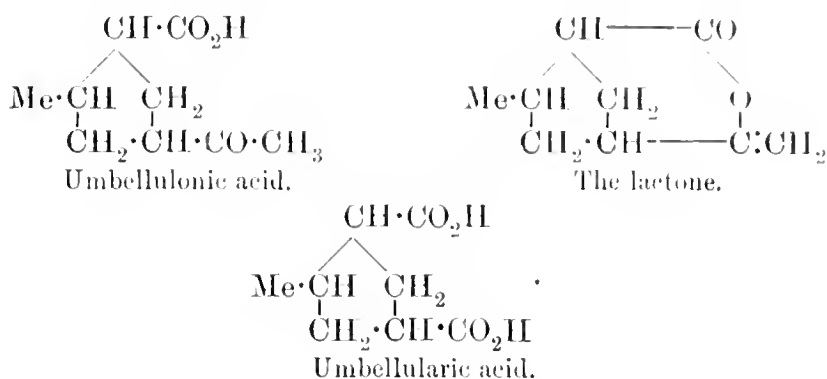
group $\begin{array}{c} x \\ \diagdown \\ \text{C} \\ \diagup \\ y \end{array} \begin{array}{l} \text{CH}_3 \\ \text{H} \end{array}$, which is contained in this compound, but not in norpic acid.

Umbellulone is therefore most probably represented by the formula



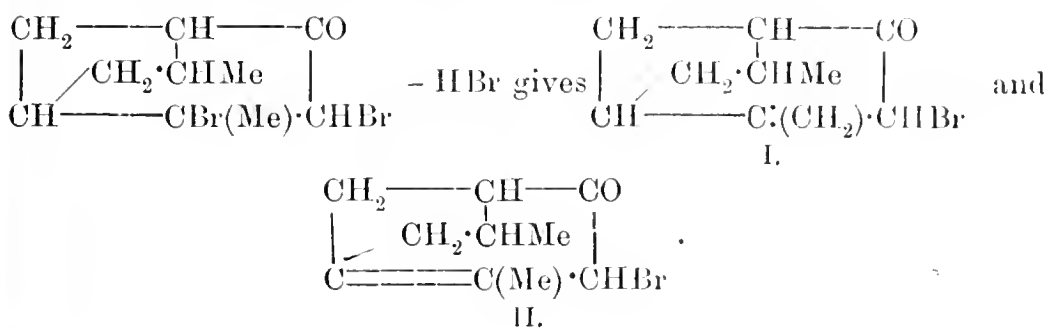
That is, "an $\alpha\beta$ -unsaturated cyclic ketone containing two closed rings," as was indicated by the observations of Power and Lees (*loc. cit.*).

The products obtained by the oxidation of umbellulone would then have the following constitution :

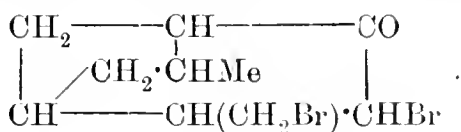


The above constitutional formula offers a ready explanation of the behaviour of umbellulone on treatment with bromine and subsequent distillation of the product.

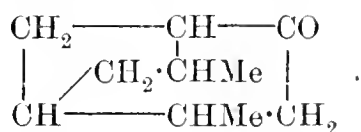
The liquid obtained by the treatment of umbellulone with bromine represents the compound formed by the direct addition of the halogen to the carbon atoms of the ethylenic linking. This compound, on distillation, eliminates hydrogen bromide in two ways:



One of these unsaturated compounds (probably II) is incapable of recombining with the hydrogen bromide, and represents the monobromoumbellulone. The other compound immediately unites with the elements of hydrogen bromide, and yields the solid dibromodihydro-umbellulone, which is therefore probably represented by the formula



The saturated ketone, $\text{C}_{10}\text{H}_{16}\text{O}$ (m. p. of semicarbazone, 177°), obtained by Lees by the reduction of monobromoumbellulone, $\text{C}_{10}\text{H}_{13}\text{OBr}$, and which it is proposed to name *α-dihydroumbellulone*, will therefore be represented by the formula



By the reduction of umbellulone itself with sodium and alcohol and

subsequent oxidation of the resulting alcohol with a limited amount of chromic acid, a ketone, $C_{10}H_{16}O$ (m. p. of semicarbazone, $155-156^\circ$), is obtained, for which the name *β -dihydroumbellulone* is proposed. This ketone has an odour almost indistinguishable from that of pulegone, and is unsaturated; it is evident, therefore, that when umbellulone is reduced by sodium and alcohol, the ethylenic linking remains unattacked, whilst one of the carbon rings becomes ruptured by the addition of two atoms of hydrogen.

The rupture of one of the closed rings contained in bromodihydroumbellulone, $C_{10}H_{15}OBr$, was shown by Lees to take place when this compound is reduced by sodium and alcohol, but the "tetrahydroumbellulol" obtained is undoubtedly a mixture, as the ketone resulting from its oxidation yielded semicarbazones of m. p. 150° and 171° respectively. It is impossible to say whether this mixture consists of structural or only stereo-isomerides.

EXPERIMENTAL.

The umbellulone employed in this investigation was obtained from the essential oil of *Umbellularia Californica*, which had been specially distilled for this purpose. It was found to have the following constants: $d = 0.9453$ at $20^\circ/20^\circ$; $\alpha_D - 21^\circ 55'$ in a 1-dcm. tube.

Two thousand grams of this oil were freed from acids and phenols by shaking with potassium hydroxide, after which the washed and dried oil was submitted to a prolonged fractional distillation, and the following fractions were eventually collected. Below 190° , $190-200^\circ$, $200-215^\circ$, $215-225^\circ$, $225-235^\circ$, $235-245^\circ$, $245^\circ +$.

The fraction $215-225^\circ$ weighed 580 grams; it had $\alpha_D - 34^\circ 4'$ in a 1-dcm. tube, and a specific gravity of 0.9600 at $15^\circ/15^\circ$. On treatment with semicarbazide, it gave from 50-60 per cent. of the theoretical yield of semicarbazidodihydroumbellulonesemicarbazone (m. p. 216°), and evidently represented fairly pure umbellulone. Except where otherwise stated, this fraction boiling from $215-225^\circ$ was the "umbellulone" used throughout this investigation.

Oxidation of Umbellulone with Potassium Permanganate.

One hundred and twenty grams of umbellulone were shaken into an emulsion with 1500 c.c. of water and the mixture cooled by the introduction of powdered ice. A 4 per cent. solution of potassium permanganate was then gradually added, with vigorous shaking, until the pink colour produced was only slowly discharged.

In this manner, it was found that an amount of permanganate equivalent to rather less than four atomic proportions of oxygen was

required. After removing the manganese dioxide, the liquid was concentrated, and a small amount of non-volatile, neutral products removed by shaking with ether; the aqueous liquid was then made strongly acid by the addition of sulphuric acid, the precipitated acids extracted with ether, and the ethereal solution washed and dried. On removing the ether, an oil was obtained which was found to be entirely soluble in cold sodium carbonate solution.

Formation of the Unsaturated Lactone, $C_9H_{12}O_2$.

The acids obtained by the oxidation of the umbellulone were then slowly distilled under 20 mm. pressure, when the portion of the distillate which passed over below 180° formed a fairly mobile liquid, whilst that which boiled above this temperature was a very viscous, brown syrup. The whole of the distillate was dissolved in ether, the ethereal liquid shaken several times with sodium carbonate solution, washed, dried, and the ether removed. The residue was a pale yellow, mobile oil having a pleasant odour; when distilled under atmospheric pressure, it nearly all (35 grams) passed over between 217° and 220° , and was evidently identical with the lactone obtained by Lees (*loc.cit.*).

0.1647 gave 0.4356 CO_2 and 0.1192 H_2O . $C = 70.96$; $H = 7.91$.

$C_9H_{12}O_2$ requires $C = 71.05$; $H = 7.88$ per cent.

This lactone was found to have the following constants: b. p. $129-133^\circ/50$ mm. and $99-100^\circ/15$ mm.; $d = 1.0197$ at $20^\circ/20^\circ$; α_D (without solvent) $-53.4'$ in a 25 mm. tube, whence $[\alpha]_D - 210.58^\circ$.

It is unsaturated, since it instantly decolorises a solution of bromine in chloroform, and, as it is readily oxidised by cold potassium permanganate, it is evident that the ethylenic linking contained in it must have been produced during the distillation of the products of oxidation.

Hydrolysis of the Lactone, $C_9H_{12}O_2$, and Formation of a Saturated Keto-acid, $C_9H_{14}O_3$.

Five grams of the lactone were dissolved in an excess of alcoholic potassium hydroxide and the mixture boiled for a few minutes. This liquid was then poured into water and acidified with sulphuric acid, after which it was extracted with ether and the ethereal solution washed, dried, and evaporated, when an almost colourless, viscous liquid was obtained.

This substance distilled at $193-195^\circ/50$ mm., and was a saturated compound, since it did not decolorise a dilute solution of bromine in chloroform.

0.1544 gave 0.3579 CO_2 and 0.1173 H_2O . $\text{C} = 63.22$; $\text{H} = 8.44$.

$\text{C}_9\text{H}_{14}\text{O}_3$ requires $\text{C} = 63.52$; $\text{H} = 8.23$ per cent.

The empirical formula of this acid, $\text{C}_9\text{H}_{14}\text{O}_3$, agrees with that of the hydroxy-acid which would have been expected to be produced by the hydrolysis of the lactone, $\text{C}_9\text{H}_{12}\text{O}_2$, but it is evident that it cannot be this compound, as it is saturated, whereas the lactone from which it is derived is unsaturated.

On treatment with hydroxylamine, this acid readily yields a crystalline oxime melting at $169-170^\circ$; it is therefore a keto-acid, and was, in fact, found to be identical with the umbellulonic acid subsequently described, from which it will be seen that the lactone is derived.

Examination of the Acids formed by the Oxidation of Umbellulone.

The acids which had been removed from the ethereal solution of the lactone by shaking it with sodium carbonate were liberated by the addition of sulphuric acid and extracted with ether. On removing the ether, a brown liquid was obtained, which consisted of a mixture of acids, and it was observed that when this was distilled under 20 mm. pressure it yielded a further quantity of lactone. This mixture of acids was dissolved in absolute ethyl alcohol, and esterified by passing dry hydrogen chloride through the boiling liquid for three hours. The esters were then precipitated by the addition of water and extracted with ether, the ethereal liquid freed from acids by shaking with sodium carbonate solution, washed, and dried. On removing the ether, a nearly colourless liquid was obtained, which was distilled under 20 mm. pressure, and the following fractions collected: $125-135^\circ$, $135-165^\circ$, $165-176^\circ$.

Isolation of Umbellulonic Acid.—The fraction $125-135^\circ$ was the largest, and had a pleasant odour. It was distilled under the ordinary pressure, when the greater portion passed over as an almost colourless liquid at $237-241^\circ$, the temperature being most constant at $238-239^\circ$.

0.1326 gave 0.3236 CO_2 and 0.1085 H_2O . $\text{C} = 66.56$; $\text{H} = 9.09$.

0.1326 „ 0.3237 CO_2 „ 0.1086 H_2O . $\text{C} = 66.58$; $\text{H} = 9.10$.

$\text{C}_{11}\text{H}_{18}\text{O}_3$ requires $\text{C} = 66.66$; $\text{H} = 9.09$ per cent.

This ester was then hydrolysed and the acid extracted with ether in the usual manner. After removal of the ether, a nearly colourless, viscous liquid was obtained, which, after standing for some time, became solid. When crystallised from light petroleum, it separated in colourless prisms melting sharply at 102° .

0.1031 gave 0.2412 CO_2 and 0.0770 H_2O . $\text{C} = 63.80$; $\text{H} = 8.29$.

$\text{C}_9\text{H}_{14}\text{O}_3$ requires $\text{C} = 63.53$; $\text{H} = 8.23$ per cent.

This compound has been designated *umbellulonic acid*.

Umbellulonic acid dissolves sparingly in cold, but more readily in hot water. It is moderately soluble in ether and light petroleum, from which it can be crystallised, and is extremely soluble in the other ordinary organic solvents. A determination of its optical rotatory power gave the following result:

0.5343 dissolved in 25 c.c. of chloroform gave $\alpha_D +16^{\circ}8'$ in a 2-dem. tube, whence $[\alpha]_D +377.6^{\circ}$.

The fact that umbellulonic acid is a keto-acid is shown by the following experiment: half a gram of the acid was dissolved in an excess of potassium hydroxide and 0.3 gram of hydroxylamine hydrochloride added. After allowing the mixture to stand overnight, it was acidified with sulphuric acid, when a substance was precipitated which rapidly became solid. This, when recrystallised from ethyl acetate, was obtained in the form of minute, colourless prisms, which melted with decomposition at $169-170^{\circ}$. This substance was evidently the oxime of umbellulonic acid, and was identical in all respects with the oxime of the keto-acid obtained by the hydrolysis of the lactone.

0.1118 gave 0.2388 CO_2 and 0.0843 H_2O . $\text{C} = 58.25$; $\text{H} = 8.37$.

$\text{C}_9\text{H}_{14}\text{O}_2\text{:NOH}$ requires $\text{C} = 58.37$; $\text{H} = 8.11$ per cent.

As umbellulonic acid is the principal constituent of the mixture of acids obtained by the oxidation of umbellulone, and is also obtained by the hydrolysis of the lactone which is formed on distillation of this mixture, it would appear probable that this acid is the parent substance of the lactone; or, in other words, that the unsaturated lactone is formed by the elimination of water from the enolic modification of umbellulonic acid. If this supposition is correct, it would be expected that umbellulonic acid on distillation would pass to some extent into the lactone, and this was found to be the case.

Conversion of Umbellulonic Acid into the Lactone.—About 15 grams of umbellulonic acid were slowly distilled under 50 mm. pressure, when it was observed that some water was eliminated. The distillate was again distilled, then dissolved in ether, and the ethereal liquid, after being freed from acid by repeatedly shaking with sodium carbonate solution, was washed and dried. On evaporating the ether, a few grams of a mobile oil having the odour of the lactone were obtained. This was distilled under the ordinary pressure, when a liquid boiling from $218-221^{\circ}$ was obtained, which was found to be identical with the lactone formed on distillation of the original mixture of acids prepared by the oxidation of umbellulone.

0.1236 gave 0.3222 CO_2 and 0.0919 H_2O . $\text{C} = 71.09$; $\text{H} = 8.26$.

$\text{C}_9\text{H}_{12}\text{O}_2$ requires $\text{C} = 71.05$; $\text{H} = 7.89$ per cent.

The proportion of the lactone thus obtained from the pure keto-acid was not so great as that given by the distillation of the original mixture of acids. It would therefore appear that the greater yield of lactone initially obtained is due to the influence of the other acids with which the umbellulonic acid is associated when first produced; these other acids having a higher boiling point, and some of them apparently giving rise to anhydrides. The correctness of this explanation is evident from the fact that these acids, when free from umbellulonic acid, yield no lactone on distillation, but, if again mixed with the keto-acid and distilled under suitable conditions, as much as 40—50 per cent. of the latter is converted into the lactone.

Examination of the Acids of Higher Boiling Point.—The fraction of esters boiling at 135—165°, prepared from the oxidation acids as previously described, was only small in amount. It evidently consisted of a mixture of substances, as it was found impossible to obtain from it any ester of constant boiling point.

The fraction of esters boiling at 165—176° was larger than the preceding one. It was fractionally distilled under 20 mm. pressure, when the greater portion passed over between 173° and 176°, principally at 174°, as a pale yellow oil having a very faint odour. On analysing this liquid, results were obtained which were not in agreement with any possible formula, and it therefore appeared to be a mixture of substances, although it distilled at such a constant temperature. It was hydrolysed by boiling with alcoholic potassium hydroxide, and the acids extracted with ether in the usual manner. On evaporating the ether, a rather viscid, brown oil was obtained, which, on standing for some weeks, became partially crystalline; it was spread on a porous tile and allowed to drain. The solid thus obtained was dissolved in benzene, the solution filtered, concentrated, and allowed to cool. The crystalline substance which separated was removed by filtration, well washed with benzene, and recrystallised from a large volume of this solvent, when it was obtained in nearly colourless, needle-shaped crystals melting at 164°. It was finally recrystallised from water, in which it is nearly insoluble in the cold, and was then obtained in large, colourless, needle-shaped crystals, which melted at 165° and sublimed without undergoing change.

0.1035 gave 0.2527 CO₂ and 0.0624 H₂O. C = 66.59; H = 6.70.

0.1132 „ 0.2774 CO₂ and 0.0700 H₂O. C = 66.83; H = 6.87.

C₁₀H₁₂O₃ requires C = 66.66; H = 6.66 per cent.

This acid cannot be derived from umbellulone; it is a saturated compound, and would therefore appear to be a benzene derivative. So far as can be ascertained, it is not identical with any compound hitherto described, and its formation would seem to indicate the

presence in the essential oil of Californian Laurel of a substance which has not been identified.

The benzene mother liquors from this acid yielded a quantity of α -homopiperonylic acid, which was undoubtedly derived from the safrole contained in the original oil (Power and Lees, *loc. cit.*). Although other acids were certainly present in this mixture, and also in that obtained from the fraction of esters boiling at 135—165°/20 mm., they could not be separated. By the oxidation of umbellulone under the conditions employed, no derivative other than umbellulonic acid could therefore be isolated.

Oxidation of Pure Umbellulone.—Thirty grams of the umbellulone fraction were treated with semicarbazide, the resulting semicarbazido-semicarbazone washed with ether until free from adhering oil, then decomposed with dilute sulphuric acid, and the regenerated umbellulone isolated. This was subsequently oxidised with potassium permanganate under the same conditions as were employed when oxidising the umbellulone fraction of the oil. The resulting acids yielded some lactone on distillation, and, when converted into their ethyl esters, gave ethyl umbellulonate and a comparatively small proportion of a mixture of esters which distilled from 135—172°. Umbellulonic acid, therefore, is not the only product of the oxidation of umbellulone.

Oxidation of the Lactone. Formation of Umbellularic Acid.—Thirty grams of the pure lactone were shaken into an emulsion with 600 c.c. of water, and a 4 per cent. solution of potassium permanganate gradually added with constant shaking, the mixture being kept cool by immersion in cold water. When an amount of permanganate equivalent to four atomic proportions of oxygen had been added, the pink colour was no longer discharged. A moderate excess of the oxidising agent was then added, and the mixture allowed to stand for some hours, when apparently no more potassium permanganate became decolorised. The excess was then removed by means of sulphurous acid, and the precipitated manganese dioxide was separated by filtration. The liquid was subsequently concentrated to a small bulk, acidified with sulphuric acid, and repeatedly extracted with ether; the ethereal liquid was then washed, dried, and the ether removed. The residue was an almost colourless syrup, which, after standing for a few hours, became entirely crystalline.

When fractionally crystallised from benzene, this acid was found to be homogeneous, as all the fractions yielded colourless prisms which melted sharply at 120—121°.

0.1062 gave 0.2176 CO₂ and 0.0661 H₂O. C=55.88; H=6.91.

C₈H₁₂O₄ requires C=55.81; H=6.98 per cent.

0.5111 dissolved in 25 c.c. of chloroform had α_D , -3°40' in a 2-dm. tube, hence $[\alpha]_D$, -89.7°.

This acid has been designated *umbellularic acid*, and, for reasons which have been fully discussed in the introductory portion of this paper, it is probably 1-methylpentamethylene 3:5-dicarboxylic acid.

Umbellularic acid is moderately soluble in benzene and almost insoluble in light petroleum, but dissolves with great readiness in the other ordinary organic solvents. When crystallised from water, in which it is moderately soluble, it separates in needle-shaped crystals, which melt at 85° and contain one molecule of water of crystallisation.

0.6586 of the acid which had been crystallised from water and dried in the air, when heated for two hours at 100° , suffered a decrease in weight equivalent to 10.1 per cent.; one molecule of water requires a loss of 9.4 per cent. On further heating, it continued slowly to decrease in weight, owing to sublimation. The hydrated acid was analysed:

0.0975 gave 0.1760 CO_2 and 0.0635 H_2O . $\text{C} = 50.16$; $\text{H} = 7.37$.

$\text{C}_8\text{H}_{12}\text{O}_4 \cdot \text{H}_2\text{O}$ requires $\text{C} = 50.52$; $\text{H} = 7.37$ per cent.

When umbellularic acid is heated to about 150° , water is eliminated, with the formation of the anhydride.

Umbellularic anhydride is a colourless liquid, which distils at $167\text{--}169^{\circ}/50$ mm., and on boiling it with water umbellularic acid is regenerated.

0.1342 gave 0.3061 CO_2 and 0.0800 H_2O . $\text{C} = 62.21$; $\text{H} = 6.62$.

$\text{C}_8\text{H}_{10}\text{O}_3$ requires $\text{C} = 62.34$; $\text{H} = 6.49$ per cent.

The umbellularic acid was esterified by boiling it with an excess of absolute ethyl alcohol containing a small proportion of sulphuric acid, but only a relatively small yield of ester could be obtained.

Diethyl umbellularate is a colourless liquid, possessing a fruity odour, and distils at $158\text{--}160^{\circ}/50$ mm.

0.1335 gave 0.3077 CO_2 and 0.1078 H_2O . $\text{C} = 62.86$; $\text{H} = 8.97$.

$\text{C}_{12}\text{H}_{20}\text{O}_4$ requires $\text{C} = 63.16$; $\text{H} = 8.77$ per cent.

Umbellularic acid is a very stable substance. It is not appreciably oxidised by potassium permanganate at 60° , and is recovered unchanged after boiling for ten hours with eight times its weight of a mixture of three parts of fuming nitric acid and one part of water. After boiling for five hours with undiluted fuming nitric acid, besides unchanged umbellularic acid, only a trace of oxalic acid could be identified. It is unaltered by heating with concentrated hydrochloric acid at 190° for five hours. An attempt was made to prepare a bromoumbellularic acid by heating together the dry acid, red phosphorus, and bromine in the requisite proportions, but after the formation of the acid bromide

was complete only a very slight action occurred. The mixture was heated on the water-bath for two hours, then treated with ethyl alcohol, and the resulting esters freed from bromine. On distillation, these esters were found to boil between 90° and $180^{\circ}/20$ mm., but the greater portion passed over at the boiling point of ethyl umbellularate, and only contained a trace of bromine. It was therefore not found possible to obtain a bromoumbellularic acid from the amount of material available.

Bromination of Pure Umbellulone.

Forty grams of the umbellulone fraction were treated with semicarbazide, and the resulting semicarbazido-semicarbazone washed with ether until free from adhering oil, after which it melted at 216° and was evidently pure. It was then decomposed with dilute sulphuric acid and the regenerated umbellulone isolated. This was then dissolved in chloroform and treated with bromine in the manner described by Lees (*loc. cit.*). The resulting dibromide was then distilled under 20 mm. pressure, when it yielded products identical with those obtained by Lees by the bromination of the umbellulone, namely: a limpid liquid boiling below $130^{\circ}/20$ mm.; a heavy, pale yellow oil (b. p. $140-145^{\circ}/20$ mm.) having a very pungent odour; and the solid dibromodihydroumbellulone (m. p. 119°).

The liquid boiling at $140-145^{\circ}/20$ mm. was analysed:

0.1482 gave 0.2826 CO_2 and 0.0775 H_2O . $\text{C} = 52.00$; $\text{H} = 5.81$.

$\text{C}_{10}\text{H}_{13}\text{OBr}$ requires $\text{C} = 52.40$; $\text{H} = 5.68$ per cent.

This unsaturated monobromoumbellulone was treated with hydrogen bromide under varying conditions, but it was found impossible to cause it to combine with the latter. When reduced with zinc dust and acetic acid, it yielded the saturated ketone, $\text{C}_{10}\text{H}_{16}\text{O}$, obtained in a similar manner by Lees (*loc. cit.*), but its semicarbazone was found to have the melting point of 177° , and not $171-172^{\circ}$, as stated by him. This ketone has been designated *α -dihydroumbellulone*.

The fraction boiling below 130° was distilled under the ordinary pressure, and afterwards over metallic sodium, when it was finally obtained as a colourless liquid boiling at $176-177^{\circ}$ and having the odour of cymene.

0.1233 gave 0.4052 CO_2 and 0.1156 H_2O . $\text{C} = 89.60$; $\text{H} = 10.42$.

$\text{C}_{10}\text{H}_{14}$ requires $\text{C} = 89.55$; $\text{H} = 10.45$ per cent.

Eighty grams of umbellulone were brominated in order to obtain a further quantity of this hydrocarbon, and about 8 c.c. of it were thus obtained. Five grams of this were oxidised by boiling for a week with a mixture of 47 grams of potassium bichromate, 65 grams of

sulphuric acid, and 200 c.c. of water. The white, insoluble precipitate which had been formed was then removed by filtration, dissolved in ammonia, the solution filtered, and the acid reprecipitated by the addition of hydrochloric acid. This precipitate was collected, well washed with hot water, and dried, after which, when heated, it sublimed without melting.

0.1108 gave 0.2340 CO_2 and 0.0375 H_2O . $\text{C} = 57.60$; $\text{H} = 3.76$.

$\text{C}_8\text{H}_6\text{O}_4$ requires $\text{C} = 57.83$; $\text{H} = 3.61$ per cent.

This substance was evidently terephthalic acid, as it gave a dimethyl ester which melted sharply at 140° . The hydrocarbon from which this acid was obtained is therefore *p*-cymene.

All the compounds obtained by Lees (*loc. cit.*) by the bromination of the umbellulone, namely, a hydrocarbon, $\text{C}_{10}\text{H}_{14}$, monobromoumbellulone, $\text{C}_{10}\text{H}_{13}\text{OBr}$, and dibromodihydroumbellulone, $\text{C}_{10}\text{H}_{14}\text{OBr}_2$, were therefore derived from the umbellulone itself, and not from any impurity contained in the fraction of oil employed.

Reduction of Umbellulone.

Twenty-five grams of umbellulone were dissolved in 100 c.c. of absolute alcohol, and 18 grams of sodium in small pieces were gradually introduced. The liquid was not cooled, but allowed to boil vigorously. When all the sodium had dissolved, the mixture was distilled in steam, and the oil contained in the distillate isolated by extracting with ether. After removal of the ether, the residual oil was found to be highly unsaturated, as it instantly decolorised a solution of bromine in chloroform. The reduction was therefore repeated, and the oil isolated in a similar manner, but it was found to be still unsaturated. It was then distilled under the ordinary pressure, when the greater portion of it was obtained as a colourless liquid, boiling at $208\text{--}210^\circ$, and having a pleasant, somewhat camphoraceous odour. This liquid was unsaturated, and on analysis gave results which indicated it to be a mixture of compounds of the formulæ $\text{C}_{10}\text{H}_{16}\text{O}$ and $\text{C}_{10}\text{H}_{18}\text{O}$ respectively.

β -Dihydroumbellulone.—Fifteen grams of the liquid boiling at $208\text{--}210^\circ$ were oxidised with a mixture of 20 grams of potassium bichromate, 17 grams of sulphuric acid, and 100 c.c. of water. After heating for about three quarters of an hour, the bichromate had become completely reduced, and the mixture was then distilled in steam. The distillate was extracted with ether, and, on removing the latter, about 6 grams of a pale yellow oil were obtained. When this was distilled under the ordinary pressure, it passed over between 204° and 209° as an

almost colourless liquid, and had an odour closely resembling that of pulegone.

0.1398 gave 0.4032 CO_2 and 0.1337 H_2O . $\text{C} = 78.66$; $\text{H} = 10.63$.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires $\text{C} = 78.95$; $\text{H} = 10.53$ per cent.

This substance was unsaturated, as it instantly decolorised a dilute solution of bromine in chloroform. It is isomeric with the α -dihydroumbellulone obtained by the reduction of monobromoumbellulone, and is therefore β -dihydroumbellulone. As only 6 grams of this ketone, $\text{C}_{10}\text{H}_{16}\text{O}$, had been obtained by oxidising 15 grams of the mixture of alcohols, $\text{C}_{10}\text{H}_{16}\text{O}$ and $\text{C}_{10}\text{H}_{18}\text{O}$, it is evident that the former alcohol must have been completely destroyed.

The oxime of β -dihydroumbellulone was prepared in the usual manner, and found to be a liquid boiling at about 130° under 25 mm. pressure. The semicarbazone of this ketone was first obtained as a liquid, but after standing for some time it became crystalline. It was recrystallised from a mixture of ethyl acetate and light petroleum, after which it melted at $155\text{--}156^\circ$.

0.1008 gave 0.2330 CO_2 and 0.0838 H_2O . $\text{C} = 63.04$; $\text{H} = 9.24$.

$\text{C}_{11}\text{H}_{19}\text{ON}_3$ requires $\text{C} = 63.16$; $\text{H} = 9.09$ per cent.

Tetrahydroumbellulone, $\text{C}_{10}\text{H}_{18}\text{O}$.

In order that tetrahydroumbellulone might be compared with the known ketones of the formula $\text{C}_{10}\text{H}_{18}\text{O}$, it was prepared by oxidising "tetrahydroumbellulol" (compare Lees, *loc. cit.*) in the usual manner.

This ketone is a colourless liquid, boiling at $197\text{--}198^\circ$, and has a pleasant, somewhat camphoraceous odour.

0.1185 gave 0.3371 CO_2 and 0.1235 H_2O . $\text{C} = 77.58$; $\text{H} = 11.58$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C} = 77.92$; $\text{H} = 11.69$ per cent.

The semicarbazone was prepared from it, and crystallised once from alcohol, when it was obtained in colourless prisms melting at 148° .

0.1161 gave 0.2662 CO_2 and 0.1060 H_2O . $\text{C} = 62.53$; $\text{H} = 10.14$.

$\text{C}_{11}\text{H}_{21}\text{ON}_3$ requires $\text{C} = 62.56$; $\text{H} = 9.95$ per cent.

On fractional crystallisation, this was found to be a mixture of isomeric semicarbazones, as substances of the melting point 171° and 150° respectively were obtained from it.

CXIV.—*Contributions to the Theory of Isomorphism based on Experiments on the Regular Growths of Crystals of One Substance on those of Another.*

By THOMAS VIFOND BARKER, B.A., B.Sc. (Oxon) (Senior Demy of Magdalen College, Oxford).

Introductory.

EXAMPLES of the regular growth of one mineral on another have long been known; they may be grouped into three classes: (1) one mineral is a paramorph of the other, so that they have the same percentage composition, for example, rutile on anatase; calcite on aragonite; hornblende on augite, and, conversely, augite on hornblende; (2) one mineral is a decomposition product of the other, in which case they have some elements in common, for instance, barytes on witherite; (3) the two minerals neither have similarity of composition nor belong to the same crystallographic system; as examples of this type, the combinations rutile on mica and tourmaline on mica may be cited. A complete list of all such occurrences has been compiled by Mügge (*Neues Jahrbuch für Mineralogie, Beilage-Band*, 1903, 16, 335).

In the examples of regular growth among minerals, it is not usually possible to confirm the observations by experiments, for it is difficult to prepare synthetically the appropriate pairs of compounds. But when we turn to soluble substances the crystallisation can be watched and controlled. It is necessary, however, that the substance which has to receive the deposit shall not be acted on by the solution containing the other. Since the best examples of insoluble crystals are found in nature as minerals, it follows that the simplest way of studying the deposition of substances on each other is to experiment with soluble salts and minerals.

Although experiments of this kind have been previously made, they were isolated and had no definite end in view. The following investigations were made in order to ascertain whether the orientating influence of one crystal on another is due to some similarity of structure. Comparative experiments may enable us to discover the requisite conditions for the formation of regular growths, and may throw some light on the crystal structure of the substances concerned.

The first experiments on regular deposition were made by Wakkernagel in 1825 (*Kastner's Archiv f. d. gesammte Naturlehre*, 1825, 5, 293), who asserted that he obtained a regular deposit of lead nitrate on alum, and of alum on boracite. He also varnished some of his crystals, and observed the same regular deposit as on an unvarnished

crystal; he was therefore of the opinion that a crystal possesses a sphere of activity ("Wirkungskreis"). A regular deposit of lead nitrate on alum from an aqueous solution of the former is *a priori* absurd, for lead sulphate is immediately formed and deposited on the alum crystal. Kopp (*Ber.*, 1882, **15**, 1653) repeated Wakkernagel's experiments, and could not obtain any regular deposition in either of the above cases; he also showed (*Annalen*, 1855, **94**, 118) that growth on a varnished crystal begins at the edges or quoins, that is, at those points which remain uncovered owing to the shrinkage of the varnish. The idea of a sphere of activity, however, was not given up immediately; Bombicci (*Mem. Acad. Bologna*, (3), **7**, 123), for example, in 1876 asserted that if a beaker containing a solution of sodium nitrate be placed on a piece of calcite, the latter exerts an "iso-orientating influence" to such a degree that the crystals of sodium nitrate appear in the beaker with their edges parallel to the edges of the calcite!

Frankenheim (*Pogg. Ann.*, 1836, **37**, 516; 1860, **111**, 1), in 1836, observed that if a drop of a solution of sodium nitrate be allowed to evaporate on a cleavage-piece of calcite, small rhombohedra appear which are definitely orientated. The edges of the rhombohedra are approximately parallel to those of the calcite-cleavage. He also tried old cleavages, and, finding that the deposition was not regular, concluded that the calcite must be freshly cleaved.

Frankenheim then proceeded to try other minerals with good cleavages and found that potassium iodide, bromide, and chloride separate out as definitely orientated equilateral triangles on a fresh cleavage-piece of mica, whereas on a glass plate they crystallise in cubes. He says "in biaxial mica one side of the triangle is always nearly parallel to one of the elasticity-axes of the mica." The deposition is regular on uniaxial micas also; the orientation of the triangles is twofold, one being derivable from the other by a rotation of 180° . The cubes which accompany these triangular forms are stated to be parallel to one another if the mica-cleavage be fresh. The corresponding sodium salts did not give regular growths. Again, sodium nitrate is deposited in similarly orientated triangles on mica and on gypsum; finally, calcium sulphate grows regularly on fresh cleavages of gypsum.

The next work was done by de Senarmont (*Compt. rend.*, 1854, **38**, 105), who obtained regular growths of sodium nitrate on certain natural faces of calcite, namely, rhombohedral forms, both steeper and fatter than the form $\{100\}$, on the hexagonal prism and the scalenohedron $\{20\bar{1}\}$.

In 1877, O. Lehmann (*Zeit. Kryst. Min.*, **1**, 490) described some 14 cases of regular growths of pairs of salts simultaneously deposited from solution.

Kopp (*Ber.*, 1879, 12, 917) somewhat later obtained regular growths of sodium nitrate on the following forms of calcite:

$$\begin{aligned} +R^3 &= \{201\} = v; & -2R &= \{111\} = f; \\ \propto R &= \{211\} = b; & -\frac{1}{2}R &= \{110\} = e; \end{aligned}$$

but Friedel (*Ber.*, 1872, 5, 483) could not obtain a parallel deposition on "prismatic crystals."

In 1871, Rose (*Ber.*, 4, 104) reported that Mitscherlich had obtained a zonal growth of sodium nitrate on dolomite from Traversella, and that he himself had observed a parallel growth by hanging a crystal of aragonite from Bilin in an aqueous solution of potassium nitrate. The latter experiment was repeated by Kopp (*loc. cit.*, p. 918) with a negative result, whereas the former observation was repeated by Tschermak (*Min. Mitth.*, 1882, 4, 118), who remarks that the zone crystals are "rarely" formed in the case of dolomite, never with chalybite or magnesite.

Zemiatshensky (*Zeit. Kryst. Min.*, 1894, 22, 77) confirmed Frankenheim's observations with regard to potassium iodide and mica, and also obtained regular growths of cubes of potassium iodide on gypsum.

Mügge (*loc. cit.*) also repeated Frankenheim's observations; he used two varieties of mica with large and small axial angle, namely, muscovite from an unknown locality and meroxene from Vesuvius. He found the regular growths with potassium chloride are more difficultly obtained than those of potassium bromide and potassium iodide. Sodium chloride, even with the addition of urea to encourage an octahedral habit, gave quite irregular growths. He was unable to trace any regularity in the growth of potassium iodide and gypsum.

Gaubert (*Bull. Soc. franç. Min.*, 1904, 27, 225) has recently observed that crystals of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ grow in regular positions on the rare minerals, uranocircite, autunite, meta-autunite, chalcilite, and metachalcilite; a face (010) of the salt is in contact with (001) of the mineral, and an edge (010) (001) of the former is parallel to either an edge (010) (001) or an edge (100) (001) of the latter.

H. B. Hartley has informed the author of an interesting case of regular growth observed by him. Triphenylmethane crystallises with one molecule of aniline, benzene, thiophen, or pyrrole, of crystallisation, in steep rhombohedra; triphenylmethane itself is orthorhombic. Sometimes regular growths are obtained in which the anhydrous substances crystallise on both ends of the rhombohedra, with the axis-*c* of the former parallel to the principal axis of the latter.

As regards the exact orientation of sodium nitrate on calcite, various contradictory results have been published. Frankenheim

gives nine positions, the most important of which are those where two faces are in contact with

- (1) An edge of each parallel,
- (2) An edge perpendicular to an edge of the calcite,
- (3) Corresponding diagonals parallel.

De Senarmont found that the diagonals only are parallel. Finally, Miers, as a result of measurements by means of his inverted goniometer, is of the opinion that a face and an edge are parallel.

(I) *Sodium Nitrate—Calcite Group.*

Parallel Growths on Fresh Cleavage-pieces of Calcite.

The method of study first used by the author was to allow drops of saturated solutions to evaporate on cleavage-pieces viewed under the microscope. Frankenheim's observation, that a cleavage-piece must be fresh to get a parallel growth, was confirmed; the rhombohedra of sodium nitrate quickly appear on the calcite, and, so far as the difference of angle allows, the orientation of the rhombohedra is exactly parallel to that of the calcite.

Sometimes some of the crystals of sodium nitrate are not parallel to the calcite, but are in twin position thereto—the twin axis is the rhombohedral zone axis [100]. It is interesting to note that, so far as the author is aware, no examples of calcite (or of sodium nitrate) twinned according to this law have been observed.

Cleavage-pieces from crystals of various habits and derived from different localities were then tried, in order to see whether the directive force varies at all. The varieties included opaque, milky, brown, argillaceous, and pink-manganiferous calcites; also dog-tooth spar and calcite from the Oxford Clay: no difference could be traced with all these varieties, a parallel growth being always obtained on a fresh cleavage surface, but never on an old one.

The only varieties which did not yield parallel growths were fibrous calcite and "Schieferspath," but it is difficult, if not impossible, to obtain a good cleavage surface in either of these varieties. Neither could a parallel growth be obtained on a specimen supposed to be "red calcite"; this, however, on analysis, was found to be a dolomite. The parallel growth of sodium nitrate is a most delicate test for calcite.

A solution of sodium nitrate, containing a little potassium nitrate, placed on calcite, gives on evaporation a parallel deposition of rhombohedral mixed crystals; the amount of potassium nitrate must be small, otherwise orthorhombic prisms of potassium nitrate containing sodium nitrate make their appearance in irregular positions. Retgers (*Zeit. physikal. Chem.*, 1889, 4, 599) has shown that sodium nitrate forms an isodimorphous series of mixed crystals with silver

nitrate, the rhombohedral crystals containing up to 52.32 per cent. molecules of silver nitrate. The author prepared mixtures by the same procedure as that followed by Retgers, and allowed the solutions to crystallise on calcite-cleavages. All the rhombohedral mixtures formed parallel growths just as readily as pure sodium nitrate; but the crystals are extremely deliquescent, and the author has not yet succeeded in obtaining reliable angular measurements. The specific gravity of the crystals increases with the increase of silver nitrate contained, that of the end-mixture having the value 2.982 (Retgers). The molecular volume calculated from this value and the "average molecular weight" of the mixture is 38.6. The crystals do not grow parallel on dolomite.

Connections between Parallel Growth and the Nature of the Cleavage Surface.

Since the growth on an old cleavage surface is irregular, experiments were made with a view to cleaning the surface to such an extent that parallel growths would be formed. It was found that water, benzene, polishing, or even grinding with water on a ground glass plate, had not the desired effect. Etching an old cleavage surface with hydrochloric or nitric acid increases the regularity of the deposit, and the number of parallel crystals seemed to increase with the duration of etching: the periods of time employed were five, thirty, eighty, and one hundred and eighty seconds. Conversely, the number of parallel crystals decreases on etching a freshly cleaved surface, and even on immersion in distilled water for a period of a week.

G. T. Beilby (*Proc. Roy. Soc.*, 1903, 72, 218) has recently shown that the structure of calcite undergoes a deformation if a cleavage surface be stroked several times in the same direction with a clean chamois-leather. When viewed with a high power, the surface seems to be unaltered, but on etching with a 0.2 per cent. solution of hydrochloric acid for ten to fifteen seconds, ridges and furrows, parallel to the direction of stroking, become visible. He has found the same to hold good for metals when polished, and is of the opinion that a crystalline surface-film flows and becomes amorphous. The effect of the above deformation on the subsequent growth of sodium nitrate was studied, and it was found that the change due to stroking, with or without subsequent etching, is not of such a fundamental character as to prevent the parallel deposition of crystals; no difference between the orientating action of the stroked and the unstroked part of the surface could be detected.

Growth on a Reusch-twin of Calcite.

The effect of artificial twinning upon the glide plane $e = \{110\}$, on the subsequent growth of sodium nitrate on calcite was next studied. The sodium nitrate was deposited in parallel position on both the faces which constitute the re-entrant angle of the twin-crystal. If, however, the sodium nitrate be first deposited, and the calcite be then subjected to twinning, the crystals either fall off or retain their old orientation, as might be expected.

Magnetic Experiments.

Since calcite and sodium nitrate are both diamagnetic, experiments were made in order to see whether a magnetic field has any effect on the parallel orientation of sodium nitrate, when the calcite is placed in the position exactly opposite to that it would take up if freely suspended in the field.

Mr. H. E. Hurst kindly assisted the author in these experiments.

The magnetic field was obtained by putting the pole pieces of an electromagnet 1.5 mm. apart by means of a slip of ebonite. The crystal was then inserted between the poles. The field was measured by placing a small coil of known diameter and number of turns, connected to a D'Arsonval ballistic galvanometer, in the gap. The deflection of the galvanometer when the coil was suddenly withdrawn was noted, and from this, by standardisation of the galvanometer, the field strength was calculated and found to be 18,000 electrodynamic units. The results were all of a negative character, for it was found that the magnetic field has no effect whatsoever; nor has it any orientating effect on the crystallisation of sodium nitrate on glass or on dolomite.

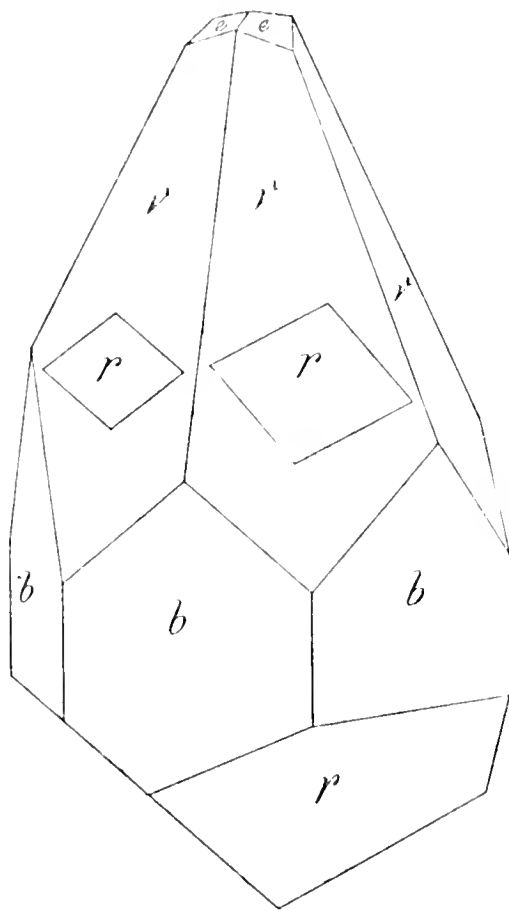
The author was afterwards made aware of the fact that Porter (*Proc. Roy. Soc.*, 1904, 73, 5) has made more elaborate experiments on the orientating action of a magnetic field on crystallo-genesis, and he also concluded that no effect could be traced.

Regular Growths on Natural Faces of Calcite.

Attempts were then made to produce regular growths of sodium nitrate on natural faces of calcite; here, of necessity, the surface is by no means clean. At first the drop-method was used, but no regular growths could be obtained on the scalenohedron $v = \{201\}$, on $e = \{110\}$, or on the hexagonal prism $b = \{2\bar{1}1\}$, or on steep scalenohedra. Another method of deposition was therefore tried. A crystal exhibiting the forms v , b and e was hung in a hot saturated solution which was allowed to cool slowly for a week. The result was negative; but on repetition, using the same crystal, the scalenohedral faces were found

to be covered with hundreds of microscopic rhombohedra which were parallel, the crystals on all the scalenohedron faces being symmetrically arranged (Fig. 1). An edge $r:r$ of each crystal of sodium nitrate made a (mean) angle of 80° with the acute edge $v:v$. Now the angle between the edge $r:r$ and the above edge $v:v$ of the calcite is (by calculation) $78^\circ 56'$, and therefore differs by 1° only from the angle made by the edge $r:r$ of the sodium nitrate. Since the above angle is the mean of several readings which varied by 2° , and since the angles for

FIG. 1.



sodium nitrate are slightly different from those of calcite, we may say that one edge of the rhombohedron of sodium nitrate lies in the rhombohedral zone of the calcite. In addition, a rhombohedral face of the former is in contact with a scalenohedral face of the latter, consequently the other rhombohedral edges of the calcite and sodium nitrate were not parallel to one another. The form $e\{-110\}$, which terminated the crystal, was very rough and apparently corroded, and no regular growths were obtained either on it or on the faces of the form $b\{-211\}$.

Since the forms r and r both lie in the rhombohedral zones, it was

thought that other forms lying in those zones might produce a regular deposit. The best form for this investigation was the rare prism-form $a\{110\}$: a crystal with good faces of this form was thoroughly cleaned by allowing to cool in a hot saturated solution for a week. On taking it out and allowing the solution adhering to it to evaporate, small rhombohedra of sodium nitrate were obtained in a definite orientation. The forms on the calcite were a , r , and r , and the orientation was the one expected, namely, a face r of the sodium nitrate in contact with the prism a , and an edge $r:r$ parallel to the edge $a:r=r:r$ of the calcite (Fig. 2). On this crystal, no regular growths were observed

FIG. 2.



on the scalenohedron faces: it may be here remarked that the only face which never fails to give a regular growth is a fresh cleavage surface. Only crystals free from cleavage cracks were employed in this connection, as it is conceivable that minute cleavage surfaces, if present, would cause a regular deposition.

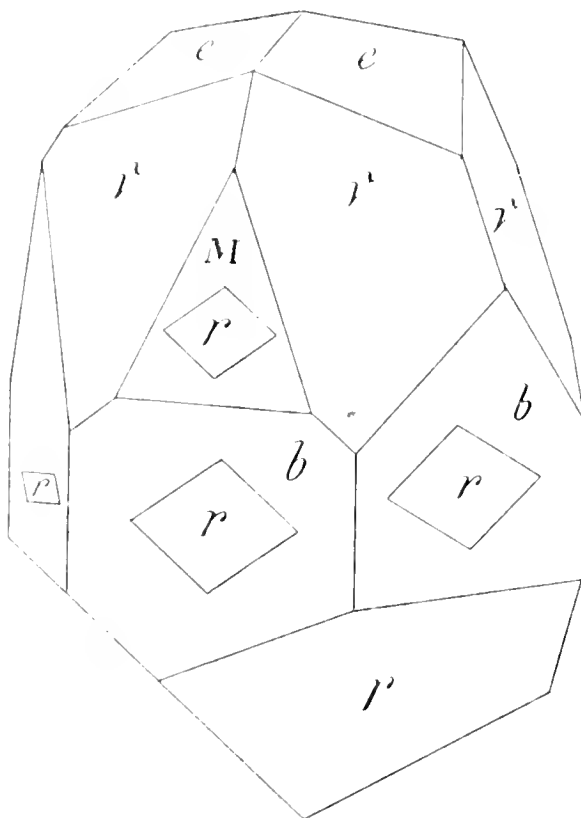
Repeated attempts were made with various crystals exhibiting the ordinary prism $b\{211\}$ to obtain regular deposits; these were for a long time uniformly unsuccessful. This led the author to the conclusion that regular growths could only be obtained on faces lying in the zones $[rr]$. The experiments were repeated later, however, with crystals from Egremont, Cumberland, which have been described by Miers (*Min. Mag.*, 1889, 2, 149) and produced a regular growth. In addition to $b\{211\}$, the crystals exhibited r , e , and a rare rhombohedral form $M=\{3\bar{1}\bar{1}\}$ or $\{04\bar{4}\}$ (Dana); bM measured = 13.5; calculated 14.13

(Fig. 3). Both the forms b and M were found to be covered with rhombohedra, so orientated that the longer diagonal of each rhomb was parallel to the edge $b:M$ of the calcite (compare Fig. 3).

Growths on the Rhombohedral Carbonates, Isomorphous with Calcite.

The other rhombohedral carbonates of the calcite group were then brought into the scope of this inquiry, and both methods, drops viewed under the microscope, and the cooling of hot saturated solu-

FIG. 3.



tions in beakers containing cleavage-pieces of the minerals, were used. Not a single case of parallel growth, however, has been obtained.

The dolomites used included pearlspar and specimens from Traversella. The chalybites included specimens from Wheal Maudlin, Alston, Aberdeen, Traversella, and Neudorf, Harz. Diallogite from Hungary, calamine from the Thüringerwald, breunnerite and rhodocrosite have all given negative results. The monoclinic, pseudorhombic baryto-calcite also induced no regular orientation.

Discussion of Parallel and Regular Growths.

The experiments on the calcite group prove conclusively that similarity of rhombohedral angle is not the predisposing cause for the

parallel deposition of sodium nitrate, for the difference between the rhombohedral angle of calcite and sodium nitrate is far greater than between sodium nitrate and the other rhombohedral carbonates.

The question immediately arises whether this is due to a difference of symmetry or of internal structure of the minerals. Now there seems to be no doubt that dolomite possesses a lower type of symmetry than calcite, for, to mention only one piece of evidence, etching figures point to the absence of the three principal planes of symmetry possessed by calcite. Dolomite therefore belongs to the diopside class (hexagonal alternating).

The question as to the symmetry of the other rhombohedral carbonates of this group is still an open one. According to Tschermak (*Anzeiger d. Akad. d. Wiss. zu Wien*, 1880, No. 19), both symmetrical and unsymmetrical etching figures are obtained by the action of hydrochloric acid on chalybite and magnesite, the latter exhibiting a greater proportion of unsymmetrical figures than the former; rhodochrosite behaves in the same way, whilst calamine gives no definite results.

The author believes that, even if some slight difference of symmetry exist, the non-formation of parallel growths cannot be attributed to that alone; because several pairs of substances have been found by him to give parallel growths, although they do not possess the same symmetry. If, for example, a drop of an aqueous solution of potassium chloride be placed on a fresh cleavage surface of rock salt, cubes of potassium chloride immediately appear in parallel position. It is certain that the cubes deposited do consist of potassium chloride, for they appear immediately, before much solution of the rock salt can have taken place, and, secondly, the two salts in question do not form isomorphous mixtures. Since rock salt appears to belong to the holohedral, potassium chloride to the holoaxial, class of the cubic system, a difference of symmetry within the system does not prevent a parallel deposition. In spite of difference of symmetry, the two structures probably possess some similarity, for the two salts possess a perfect cubic cleavage. Similarly, all the rhombohedral carbonates belong to the same system and possess many properties in common, notably a good rhombohedral cleavage; the composition, again, is similar: it may therefore be concluded that the above analogy between them on the one hand and sodium chloride and potassium chloride on the other is a legitimate one.

It is conceivable that in the case of two "isostructural" substances the actual size of the structural unit may be of the greatest importance in determining whether or not parallel deposition shall take place. Now whatever the structural unit may be, it is probable that, in an isostructural series of substances, the structural units will bear the same relations to each other as the molecular volumes.

In the rhombohedral series of carbonates, the similarity of cleavage speaks for a similarity of structure. If, therefore, cleavage rhombohedra of the members of the group be taken of such sizes that their volumes are proportional to the molecular volumes of the substances, their edges may be taken to represent the intervals between the crystal units spaced along those directions, and are known as the topic axes. The latter are calculated from the formula

$$\chi = \psi = \omega = \frac{3\sqrt{V}}{\sin 60^\circ \sqrt{C}}.$$

In consequence of the similarity of cleavage and of other physical properties, sodium nitrate may be regarded as belonging to the same isostructural series, and it is therefore possible to compare the intervals in the structure of sodium nitrate with the corresponding intervals of the rhombohedral carbonates.

The values of the ratios $c:a$ in the following list are taken from Groth's *Physikalische Krystallographie*, 3rd edition; the molecular volumes are due to Tschermak (*loc. cit.*).

Table of Axial Ratios, Molecular Volumes, and Topic Axes of the Calcite Group.

	$r:r.$	$c:a.$	$v.$	$\chi.$
(Na,Ag)NO ₃	?	?	$\left\{ \begin{array}{l} 38.6 \\ 37.8 \end{array} \right\}$?
NaNO ₃	73.30'	0.8276	37.8	4.1276
Calcite	74.55	0.8543	36.8	4.0478
(Dolomite).....	73.45	0.8322	32.1	3.9015
Rhodochrosite	73.0	0.8183	31.0	3.8781
Chalybite	73.2	0.8191	30.2	3.8432
Calamine	72.19	0.8062	28.2	3.7763

It will be seen from the above table that sodium nitrate is more nearly related to calcite than to any other member of the series both as regards molecular volume and topic axes. It therefore seems to suggest that the requisite condition for a parallel deposition is a not too great disparity of molecular volume, and, hence, of topic axes. If the distances between the structural units of two isostructural substances be greatly different, it may be expected that the structure of one will not fit into the structure of the other, and the crystals of one substance, grown on a crystal of the other, may have no definite orientation.

The regular growths of sodium nitrate on forms of calcite other than the rhombohedron are, perhaps, of greater interest than those on the rhombohedron itself. In the latter case, the whole orientation of the crystals of sodium nitrate is, as far as the small differences of angle

allow, entirely congruent with the calcite. When we consider the parallel growths of rhombohedra of sodium nitrate on other forms of calcite, it is at once seen that the only possible congruence is that of a similar edge or zone axis, for the faces of contact are of necessity dissimilar.

In the case of the regular growths on the two forms $a\text{-}\{110\}$ and $v\text{-}\{2\bar{1}0\}$, a rhombohedral zone axis was congruent, and the faces of the above two forms themselves lie in the rhombohedral zones. On the other hand, with the forms $b\text{-}\{211\}$ and $M\text{-}\{311\}$, the crystals of sodium nitrate were so orientated as to bring the edge $b:M$, the axis of the zone $[011]$, into congruence with the corresponding edge of the calcite.

Although the line, zone axis $[bM]$, is not itself present as a crystal edge on the rhombohedra of sodium nitrate, yet it exists as a line in the face.

The results show that a coincidence of edge with edge is, perhaps, of greater importance than a coincidence of plane with plane; this derives additional confirmation from the consideration that, although the parallel growths on cleavage surfaces of calcite have apparently a similar plane in congruence, yet only one similar edge in that plane can be absolutely congruent, since the plane angles of the faces are different. Further, as mentioned previously, the rhombohedra deposited on cleavage surfaces of calcite are often in twin position to the latter, and in that case it is certain that only one similar edge is congruent, namely, the twin axis.

The distances apart of the structural units in the directions of the rhombohedral edge are given by the above values for χ . Again, from the formula $\xi = 2\chi \cdot \sin \frac{\theta}{2}$, where θ is the plane rhombohedral angle, the distances apart along the edges $b:M$ may be calculated. These values for sodium nitrate and calcite are, respectively, 6.4506 and 6.2878, and it is seen that they are very close.

In the above experiments, regular growths of rhombohedra of sodium nitrate were ultimately obtained on all the forms of the calcite crystals, with the exception of the form $c\text{-}\{110\}$, the faces of which were always corroded. The question arises whether regular growths could be obtained on any form of calcite whatsoever, provided, of course, the crystal be thoroughly cleansed, so as to lay bare the unimpaired structure. The answer may be in the affirmative, because a similar direction can always be found in the rhombohedral face and in the face of the form in question. This similar direction is, of course, given by the edge of intersection of the two planes.

(II) *The Potassium Perchlorate—Barytes Group.*

The experiments on sodium nitrate and the calcite group had led to the suspicion that in such a group the parallel growth is not conditioned by the similarity of axial ratios (or of the angular measurements) alone : since if this were so, the sodium nitrate would crystallise in parallel position with more facility on chalybite than on calcite, whereas we have seen that the converse holds. The group is somewhat unsatisfactory, for only the mineral, and not the substance deposited, can be varied. Attempts were made to find a group of minerals isostructural with a series of isomorphous salts and possessing, if possible, good cleavages. It was at last found that the perchlorate and permanganate of potassium are remarkably like the barytes group of minerals. Preliminary experiments having proved that the former salt is regularly deposited on barytes from aqueous solution, the author resolved to study the growth of all substances isomorphous with that salt on the minerals celestine and anglesite, which are strictly isomorphous with barytes, and, in addition, on anhydrite.

Crystallography of the Perchlorates and Permanganates.

The permanganates of potassium, rubidium, caesium, and ammonium have already been described by Muthmann (*Zeit. Kryst. Min.*, 1894, 22, 527), whilst of the perchlorates the potassium salt was previously measured by Groth (*Ann. Phys. Chem.*, 1868, 133, 193) and the ammonium salt by Mitscherlich (*Ann. Phys. Chem.*, 1832, 25, 300). Rubidium and caesium perchlorates have not previously been measured. The following is a brief account of the perchlorates and permanganates ; a more complete description will appear shortly.

Preparation and Analysis of the Perchlorates.

The source of all the perchlorates was the commercially pure potassium salt, which was submitted to several recrystallisations ; the operation is very effective with this salt owing to its slight solubility. The other salts were made by the double decomposition of solutions of barium perchlorate and the sulphate of the metal, the barium perchlorate itself being prepared from potassium perchlorate by the method given by Groth (*loc. cit.*). The sulphates of rubidium, caesium, and thallium were obtained from Merck. Perfect mutual decomposition of the metallic sulphate and the barium perchlorate was ensured by testing the solution on a glass slide viewed in a microscope. The high purity of the salts was shown by the analyses, which consisted in chlorine estimations by the Carius method. The heating

was done in two operations, each lasting four hours, the capillaries being opened at the end of the first operation in order to relieve the pressure of gas. The silver chloride was estimated gravimetrically.

Rubidium perchlorate : 0.1611 gave 0.1264 AgCl. Cl = 19.40.

RbClO_4 requires 19.18 per cent.

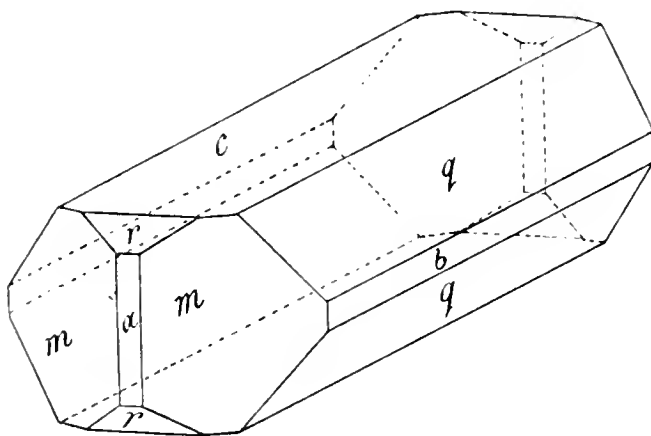
Cesium perchlorate : 0.2810 gave 0.1749 AgCl. Cl = 15.39.

CsClO_4 requires 15.26 per cent.

The isomorphous perchlorates and permanganates dealt with crystallise in the orthorhombic system and possess two very good sets of cleavage-directions, namely, parallel to the basal plane, and the prism. The indices allotted to the forms throughout the whole of this paper are those usually given to the barytes group, where the cleavage prism is $\{110\}$ and the brachydome $\{011\}$. The reasons for this were twofold : first, the salts greatly resemble the members of the barytes group of minerals, and, secondly, this orientation leads to a simplification of indices. The indices adopted by Muthmann for the permanganates lead to a value for the ratio $c : b$ which is one-half that adopted by the author.

Potassium Perchlorate.—Sixteen crystals obtained from two crops were measured. The habit was of two kinds : (1) prismatic, elongated along the axis- a (shown in Fig. 4), (2) tabular, parallel to c - $\{001\}$. The forms present were $c = \{001\}$, $q = \{011\}$, $m = \{110\}$, $r = \{102\}$, $b = \{010\}$, $s = \{111\}$, and $a = \{100\}$.

FIG. 4.

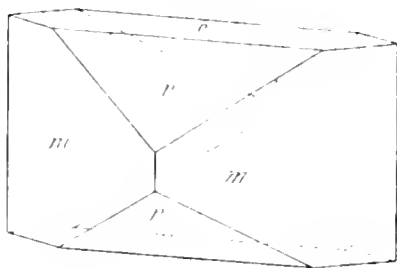


Rubidium Perchlorate.—This salt was first prepared by Longuinine (*Ann. Chem. Pharm.*, 1862, 121, 123). It is less soluble than potassium perchlorate, but very good crystals were obtained by slowly cooling hot saturated solutions ; of these, nineteen crystals selected from three crops were measured. The habit of the crystals was very

like that of the cesium salt, which is shown in Fig. 5. The forms present were $m = \{110\}$, $c = \{001\}$, $r = \{102\}$, $s = \{111\}$ and $b = \{010\}$.

Cesium perchlorate was first prepared by Setterberg (*Öfver. K. Vet. Akad. Förh.*, 1882, 6, 23). Fifteen crystals obtained from one crop were measured. The larger crystals were of the habit shown in Fig. 5, whilst the smaller ones were more elongated along the axis- b

FIG. 5.



and more tabular parallel to $c = \{001\}$. The following forms were observed: $m = \{110\}$, $r = \{102\}$, $c = \{001\}$, $s = \{111\}$ and $q = \{011\}$; s and q were rarely present.

Ammonium Perchlorate.—Several fruitless attempts to get good crystals were made, but at last a fairly good crop was obtained from a hot solution; twelve crystals were measured. The habit was slightly prismatic owing to an elongation along the axis- c . Of the forms present— $m = \{110\}$, $c = \{001\}$, $r = \{102\}$, $a = \{100\}$ and $q = \{011\}$ — m and c preponderated, r being generally small; q was only once observed.

Thallium Perchlorate.—This salt was first prepared and also measured by Roscoe (*Trans.*, 1866, 19, 504). As the author did not succeed in obtaining crystals good enough to warrant a re-measurement, the values of Roscoe are used in this paper. The crystals were slightly elongated along the axis- b , rarely the axis- c , and the forms $c = \{001\}$, $r = \{102\}$, and $m = \{110\}$ were present.

The specific gravities were determined by the method due to Retgers (*Zeit. physikal. Chem.*, 1889, 3, 289 and 497), which has been lately used by Tutton (*Trans.*, 1905, 87, 1130), and the directions given by Tutton were all observed. Methylene iodide and benzene were the liquids used. The weighings were corrected for displaced air, but the specific gravities were not reduced to a standard temperature, since the temperatures were so close to those at which Muthmann worked that a correction would only amount to one unit in the third place of decimals. Three to six determinations were made for each salt, fresh, carefully selected crystals being used each time. A single determination of the specific gravity of potassium perchlorate was

made, but the value obtained was so close to that determined by Muthmann that his number was adopted.

Following is a table of some of the more important crystallographic constants of the perchlorates and permanganates. The atomic weights used for the perchlorates were taken from the International Table for 1904, $O=16$. The data for the permanganates were taken directly from Muthmann's memoir. A table of the axial ratios is given on p. 1139.

Crystallographic Constants of the Perchlorates and Permanganates.

	$m : n$.	$c : q$.	$c : r$.	Mol. wt.	Sp. gr.	Mol. vol.
$KClO_4$	$76^\circ 1'$	$52^\circ 1'$	$39.19\frac{1}{2}'$	138.60	2.524	54.91
$RbClO_4$...	$77^\circ 5'$	—	38.57	181.85	3.014	61.33
$CsClO_4$	$78^\circ 31'$	$52^\circ 23'$	38.27	232.35	3.317	70.05
$AmClO_4$...	$76^\circ 50\frac{1}{2}'$	$52^\circ 1'$	38.55	117.49	1.952	60.19
$TlClO_4$	$77^\circ 10'$	—	38.57	303.55	4.844	62.66
$KMnO_4$...	$77^\circ 8'$	$52^\circ 24'$	$39^\circ 9'$	158.226	2.7035	58.526
$RbMnO_4$...	$79^\circ 28'$	$53^\circ 7'$	$38^\circ 13'$	201.530	3.2248	63.228
$CsMnO_4$...	$81^\circ 56'$	$53^\circ 53'$	$38^\circ 17'$	251.97	3.5974	70.642
$AmMnO_4$...	$78^\circ 28'$	$52^\circ 47'$	$38^\circ 53'$	137.144	2.2970	62.126

It is seen from the above table that all the constants of rubidium perchlorate are intermediate between those of potassium perchlorate and caesium perchlorate; again, the angles and molecular volumes of ammonium perchlorate and thallium perchlorate are very close to those of rubidium perchlorate, although the molecular weight of ammonium perchlorate is very low, whilst that of thallium perchlorate is very high. Further, since Tutton has shown that the angles of all the ammonium salts which he has investigated are very close to those of the corresponding rubidium compounds, it seems to follow that in an isomorphous series molecular weight alone does not determine the angles. The relations between the perchlorates are also seen to hold good for the permanganates. A comparison of the molecular volumes of the perchlorates and permanganates shows that the replacement of a chlorine by a manganese atom is accompanied by an increase of molecular volume in the potassium and rubidium salts and a decrease in the caesium and ammonium salts; the amount of change is greatest with the potassium and smallest with the caesium salts; this is in accordance with the fact that the relative change in the molecule is greatest with the salt possessing the lowest molecular weight.

A perusal of the tables of axial ratios given on page 1139 will prove that in both series—the perchlorates and permanganates—there is apparently a regular increase in the relative length of the axes a and c with regard to b , and also of the ratio of a to c , on replacing potassium by the heavier atom rubidium, and the latter by the still heavier atom caesium; in other words, there is a regular progression

of the ratios of the axes with molecular weight : but the values of the ammonium salts lie between those for the potassium and rubidium salt, and approximate more closely to the latter than the former. Again, the values for thallium perchlorate are almost identical with those for rubidium perchlorate. Finally, the ratios $a:b$ and $c:b$ of any permanganate are greater than those of the corresponding perchlorate.

Structure and Topic Axes.

The axial ratios of a series of isomorphous salts like the perchlorates and permanganates are not strictly comparable, since they only express, for each salt, the relative lengths of the axes- a and $-c$ with regard to the axis- b ; the ratio to each other of the b -axes of any two salts, however, is unknown. Now, by cleaving a crystal of any member of the group along the planes c and m , a parallelepipedon could be obtained such that its height and diagonals are proportional to the lengths of the crystallographic axes- c , $-a$, and $-b$ respectively. Moreover, if cleavage parallelepipeda of the perchlorates and permanganates, derived as above, be taken of such sizes that their volumes are proportional to the molecular volumes of the substances, they may be taken to represent the elementary cells at whose corners eight crystal-units are situated, whilst no such units are contained within the cells; their edges may, therefore, be taken to represent the intervals between the crystal-units measured along those directions, and are the topic axes. A table of the topic axes of the perchlorates and permanganates is given on page 1142, from which it is evident that the values of the topic axes of each rubidium salt lie between the corresponding values of the potassium and caesium salt, whilst the thallium and ammonium salts are very close to the rubidium salts. The replacement of the chlorine by the manganese atom generally effects an increase in the values of the topic axes.

It is obvious from the above that the degree of isomorphism between the perchlorates and permanganates is very close and quite comparable with that exhibited by, say, the metallic sulphates and selenates. Now, perhaps the chief evidence in favour of placing the element manganese in the seventh group of the periodic classification is derived from the close relationship of the permanganates and the perchlorates; and not the least important conclusion of the above work is, that this evidence, so far as it goes, is of the strongest possible kind. It may be added that the perchlorates and permanganates exhibit two other important properties possessed by isomorphous substances : namely, the formation of parallel growths and of mixed crystals.

Experiments on the Deposition of Potassium Perchlorate and Potassium Permanganate on the Barytes-minerals.

As mentioned above, the first regularity in growth noticed was that crystals of potassium perchlorate are deposited from aqueous solutions on barytes in regularly orientated positions. The deposition is regular on both cleavages, namely, parallel to c and m .

The following points are worthy of notice. On the c -cleavage, the small crystals of potassium perchlorate are bounded by the pinacoids a and b , the prism- m being but slightly developed when not entirely absent; in the case of the macroscopic crystals of potassium perchlorate measured, on the other hand, the prism is the dominant form in the zone $[001]$. The face of contact is $c\{001\}$, as was subsequently proved by the goniometrical measurement of large crystals grown on the basal cleavage of barytes. The edges ca , cb of the crystals of potassium perchlorate were parallel to the extinction directions of the barytes, and therefore bisected the prism angles of the latter.

The microscopic crystals deposited on prism-cleavages of barytes had each a prism face in contact; the boundaries of the crystals were the traces of the form c , a pair of prism faces, and $s\{111\}$; the edges $c:m$ were congruent. The crystals of potassium perchlorate, therefore, are entirely parallel with the crystals of barytes, in so far as the small differences of angles will allow.

The same was found to be true for cleavage-pieces of celestine; good cleavages of anglesite were not available.

Potassium permanganate also gave regularly orientated crystals on the basal and prismatic cleavages of barytes. The crystals appeared to be combinations of $a\{100\}$, $m\{110\}$ and $c\{001\}$, and were generally elongated along the axis- b ; by illuminating the slide from above, however, it was seen that the crystals are really combinations of the above forms together with $r\{102\}$. The edges $c:m$ were always parallel to the corresponding edges $C:M$ of the barytes.

The progress of growth on the prism-cleavage was very interesting: the potassium permanganate began to crystallise in small isosceles triangles, the bases of which were all parallel to the edge $M:M$ of the barytes. The mean value for the interior vertical angle was 51° ; the triangles grew in the direction of the base, and, in general, developed three new sides, thus becoming elongated, six-sided crystals. The orientation here is identical with that of the barytes, for the above interior angle, calculated on the supposition that the faces are r and c —the crystal lying on m —is $53^\circ 49'$, which is sufficiently close to the microscope-reading.

In two or three cases it has been observed that two crystals,

joined together, have, on further growth, given rise to one of the above-mentioned isosceles triangles. Such pairs of crystals would seem to be twinned on the face $C\{001\}$ (if C is really not a plane of symmetry), but their opacity renders optical experiments impossible, and prevents a further examination; on the other hand, no macroscopic twin-crystals of the perchlorates or permanganates have been observed.

The growths of potassium permanganate are also parallel on basal cleavages of celestine. The prism-cleavage of the latter mineral is not so good as that of barytes, and it was found that the growths of potassium permanganate on this cleavage are generally irregular; whether this is due to the rough surface, or to another cause hereafter mentioned, has not been settled.

Drops of solutions of the perchlorates of rubidium, caesium, ammonium, and thallium, and permanganates of rubidium, caesium, ammonium, and barium were then allowed to evaporate on cleavage flakes of barytes and celestine, and a parallel growth of ammonium permanganate was once observed on a basal cleavage of barytes; in none of the other cases was a definite orientation noticeable.

An account of the forms noticed on the crystals of the various salts is given below.

RbClO_4 :—Generally simple combinations of the basal plane and the prism, a microscope-reading of the prism-angle gave 79° ; a few crystals were elongated like the crystals of potassium permanganate along the axis- b .

CsClO_4 :—Often feathery aggregates, but a very few thin plates were measureable, and gave a reading of 80° for the prism-angle.

TlClO_4 :—Exhibited the forms c , r , m , and rarely q ? $m : m = 77\frac{1}{2}^\circ$.

AmClO_4 :—Very similar to thallium perchlorate.

RbMnO_4 :—Very similar to potassium permanganate.

CsMnO_4 :—Some crystals were obviously lying on the c -face, $m : m = 82^\circ$; r and s were also noticed.

AmMnO_4 :—The habit was the same as that of potassium permanganate: the growths observed on m - and c -cleavages of celestine, and on the m -cleavage of barytes, were never parallel; this was generally true of the c -cleavage of barytes also. In one case of the latter, however, eight small crystals, near to each other, were found to be parallel; all the remaining crystals (above 100 in number) were totally irregular. Further attempts to obtain a parallel growth on many other cleavage-pieces were fruitless.

$\text{Ba}(\text{MnO}_4)_2$:—Was also irregular (orthorhombic "cubes").

Solutions in all proportions of potassium perchlorate and permanganate deposited regularly orientated mixed-crystals on barytes without exception.

Further attempts were made to obtain parallel growths by immersing cleavage-pieces of the barytes-minerals in hot saturated solutions of the various salts, and allowing to cool slowly. Beautiful, large crystals of potassium perchlorate have thus been obtained, grown on the *c*- and *m*-cleavages of barytes and celestine, and on natural crystals of anglesite and barytes. The crystals of potassium perchlorate were always parallel to the mineral on which they were deposited. The natural crystal of barytes employed was two inches long in the direction of the *b*-axis, and exhibited the forms *r*, *m*, and *c*; and the crystals of potassium perchlorate, deposited on all these forms, had the same orientation as the barytes, the faces of contact being *r*, *m* and *c* respectively. The crystal of anglesite was not so good, but measurement on the two-circle goniometer proved that the crystals grown on it were parallel with itself.

The perchlorates of rubidium, caesium, ammonium, and thallium and permanganates of rubidium and caesium all failed to give definitely orientated growths. In the case of the permanganates, the cleavage-pieces were found to be covered with a scum, possibly manganese dioxide.

Growths on Anhydrite.

Anhydrite, CaSO_4 , possesses three good cleavages parallel to the three pinacoids; it is therefore not isostructural with the permanganates and perchlorates of the alkalis. Nevertheless, attempts were made to obtain regular growths on all three cleavages. The salts used with the drop method were ammonium perchlorate and the permanganates of potassium, rubidium, caesium, and ammonium; with the cooling method, the perchlorates of potassium, rubidium, caesium, and ammonium. No regular growths were obtained by either method.

Discussion of Results of Experiments on the Barytes Group.

The axial ratios of the minerals in the barytes group are:

Anglesite	$a : b : c = 0.7852 : 1 : 1.2894$
Celestine	$a : b : c = 0.7811 : 1 : 1.2830$
Barytes	$a : b : c = 0.8152 : 1 : 1.3136$

Whilst those of the salts investigated are:

	$a : b : c$		$a : b : c$
KClO_4	$0.7815 : 1 : 1.2805$	AmMnO_4	$0.8164 : 1 : 1.3168$
AmClO_4	$0.7932 : 1 : 1.2808$	CsClO_4	$0.8172 : 1 : 1.2976$
RbClO_4	$0.7967 : 1 : 1.2882$	RbMnO_4	$0.8311 : 1 : 1.3323$
KMnO_4	$0.7972 : 1 : 1.2982$	CsMnO_4	$0.8583 : 1 : 1.3705$
TiClO_4	$0.7978 : 1 : 1.2898$		

It is therefore evident that similarity of axial ratios, and the attendant similarity of angles, is not the favouring factor for a parallel deposition. Following is a table of the prism angles:

Celestine	75°58'	TlClO ₄	77°10'
KClO ₄	76 1	Barytes	78 23
Anglesite	76 17	AmMnO ₄	78 27½
AmClO ₄	76 50½	CsClO ₄	78 31
RbClO ₄	77 5½	RbMnO ₄	79 2½
KMnO ₄	77 8	CsMnO ₄	81 56

Now we have seen that potassium perchlorate will grow in parallel position on either celestine or barytes, the difference in prism angle being +0°3' and -2°22' respectively; whereas rubidium perchlorate will not grow regularly on either, the corresponding differences being +1°7' and -1°17'. Again, the difference between $m:m$ for barytes and caesium perchlorate is -8' only, and yet no regular deposition takes place.

On turning to the molecular volumes, however, we find a most remarkable connection between the similarity of the values of this constant and the formation of parallel growths.

The molecular volumes are in the following order:

Celestine, 46·8; anglesite, 48·2; barytes, 52·0; KClO₄, 54·915; KMnO₄, 58·498; AmClO₄, 60·19; RbClO₄, 61·33; AmMnO₄, 62·076; TlClO₄, 62·66; RbMnO₄, 63·415; CsMnO₄, 70·023; CsClO₄, 70·05; and one sees at once that in those cases in which parallel depositions have been observed there is a closeness in the values of the molecular volumes; for example, no salt having a greater molecular volume than that of potassium permanganate (with the exception of the isolated observation with ammonium permanganate) has offered any parallel growths on any of the minerals of the barytes group. As mentioned above, the difficulty of obtaining parallel growths of potassium permanganate on the m -cleavage of celestine may be partly due to the somewhat inferior cleavage; but it is worthy of notice that celestine has a lower molecular volume than barytes. Again, ammonium permanganate was only once obtained on barytes, never on celestine.

Hence, in the above series, it is similarity of molecular volume which determines whether there shall or shall not be parallel growth, whereas conclusions drawn from a similarity of angle alone (or of axial ratios) would be erroneous.

The conception of topic axes, suggested by Becke and employed so successfully by Muthmann and Tutton in their work on isomorphous series, embodies the relationships both of molecular volumes and axial ratios as described above under calcite; by their use, one can compare isostructural substances with each other, and draw conclusions regard-

ing the relative distances apart of the structural units, and hence the reticular densities in all planes can be calculated; further, such densities and distances apart are comparable for all isostructural members. The merit of this method especially lies in the last statement: for Bravais long ago showed how to calculate the relative distances apart of the structural units, and also the reticular densities, of an individual salt; the values so obtained for an individual salt, however, are not comparable with each other, since a different arbitrary unit—namely, $\text{axis-}b=1$ —is taken for each salt.

In order to make justifiable comparisons, one must be certain that the structure of the salts to be compared is similar. Now the extraordinary similarity of angles, cleavage, molecular volume, and, in addition, the formation of similarly orientated overgrowths, argue for a similarity of structure in the barytes group and the isomorphous series of the permanganates and perchlorates; we are therefore justified in making comparisons between the various members of these three groups; comparisons between such groups have not previously been made.

The structure of all the above substances is probably founded on the orthorhombic-prism space-lattice, for a maximum reticular density in the cleavage directions c and m is thereby obtained.

Just as the topic axes of the rhombohedral group were calculated from the cleavage rhombohedra, so in the barytes-perchlorate-permanganate series, topic axes can be calculated from the cleavage parallelepipeda formed by the forms c and m , and they enable us to compare corresponding lengths along their edges.

In the following table, ω and ξ represent corresponding lengths along the edges $m:m$ and $m:c$ respectively of the elementary parallelepipeda; χ and ψ are their diagonals: so that χ , ψ , ω , and ξ represent distances between contiguous crystal-units.

The values of χ , ψ , ω , and ξ are obtained from the formulæ:

$$\chi = \sqrt{\frac{3}{2} \frac{Va^2}{c}}; \quad \psi = \sqrt{\frac{3}{2} \frac{V}{ac}}; \quad \omega = \sqrt{\frac{3}{2} \frac{Vc^2}{a}}; \quad \text{and} \quad \xi = \sqrt{\frac{1}{2} \frac{V}{\chi^2 + \psi^2}},$$

where V is the molecular volume, a and c the axial ratios.

Since the topic axes are simple functions of the molecular volume and the axial ratios, and since the axial ratios betray far less differences than the molecular volumes, it is not surprising that the topic axes, when arranged in order of magnitude, follow, in general, the same sequence as the molecular volumes.

Topic Axes of the Potassium Perchlorate—Barytes Group.

	χ .	ψ .	ω .	ξ .
Celestine	3.5349	4.5931	5.7649	2.8980
Anglesite	3.5743	4.5520	5.8694	2.8938
Barytes	3.6509	4.7899	5.9472	3.0113
KClO ₄	3.7360	4.7878	6.1307	3.0365
KMnO ₄	3.8555	4.8360	6.2779	3.0924
AmClO ₄	3.8959	4.9117	6.2909	3.1346
RbClO ₄	3.9244	4.9264	6.3447	3.1492
AmMnO ₄	3.9757	4.8698	6.4126	3.1433
TlClO ₄	3.9964	5.0093	6.2606	3.2040
RbMnO ₄	4.0362	4.8565	6.4704	3.1574
CsClO ₄	4.1625	5.0929	6.6086	3.2888
CsMnO ₄	4.2551	4.9005	6.7161	3.2450

It is seen from the table that all the topic axes of potassium perchlorate and potassium permanganate are closer to those of the three minerals than are the topic axes of the remaining salts, which all failed to give parallel growths. Therefore, in these three groups of compounds—perchlorates, permanganates, and sulphates—as in the two rhombohedral groups studied above, a consideration of the topic axes enables one to predict which crystals are capable of growing in parallel position on each other. The result may be stated, then, as follows. In an isostructural series, those structures which are most nearly congruent, as indicated by similarity of molecular volume or of topic axes, are the structures which yield parallel growths. If this be true, then it is possible that salts such as rubidium permanganate, caesium permanganate, &c., which fail to give parallel growths on barytes, may grow in parallel position on potassium perchlorate or permanganate. Experiments fully confirming this prediction are described on page 1152.

We are now in a position to account for the insignificant part played by similarity of axial ratios (with the attendant similarity of angles) in conditioning a parallel growth; these ratios simply determine the solid and plane angles and the ratios of the lengths of the edges of the elementary parallelepipedal cell; they do not determine the volume of the same, nor do they give us the distances between contiguous crystal-units; as seen above, the latter depend rather on the molecular volumes. It follows, then, that the difference between the spacing of the crystal-units of two isostructural substances like barium sulphate and caesium perchlorate is not necessarily small, although the angles are almost identical. On the other hand, two substances like potassium perchlorate and barium sulphate may exhibit great differences in angles, and yet the spacing of their crystal-units may be almost identical.

Following is a list of mesh-areas, formed by four contiguous crystal-

units in the two planes $c\{001\}$ and $m\{110\}$ —the planes on which attempts were made to obtain parallel growths; these areas are inversely proportional to the reticular densities. The area in the plane $c\{001\}$ is equal to the product $\frac{1}{2}\chi\psi$, the value in the plane $m\{110\}$ being $\xi\omega$.

List of Mesh-areas.

	$c\{001\}$.	$m\{110\}$.		$c\{001\}$.	$m\{110\}$.
Celestine	8.1181	16.706	RbClO ₄	9.6664	19.980
Anglesite	8.1351	16.985	AmMnO ₄	9.6801	20.157
Barytes	8.7437	17.909	TlClO ₄	10.010	20.059
KClO ₄	8.9137	18.616	RbMnO ₄	9.8003	20.429
KMnO ₄	9.3225	19.414	CsClO ₄	10.600	21.734
AmClO ₄	9.5678	19.720	CsMnO ₄	10.426	21.794

The far less mesh-area in the plane $c\{001\}$ than in the plane $m\{110\}$ is in harmony with the fact that the basal cleavage is better than the prismatic.

The above two large groups of substances supplement each other admirably, for in the calcite—sodium nitrate group we have only one salt to five or six minerals, whereas in the potassium perchlorate—barytes group we have three minerals and nine salts. The results obtained from both groups are identical, and especially show the importance of molecular volumes. Topic axes, which are the axial ratios interpreted in terms of molecular volume, not only emphasise the important part played by molecular volumes, but also the comparative insignificance of similarity of angle in determining parallel depositions of isostructural substances on each other.

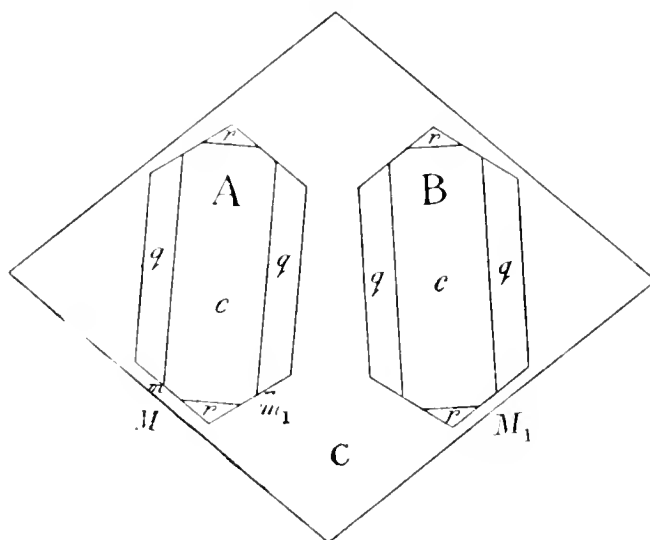
Exact Orientation of the Crystals on each other.

The crystals of the above salts cannot be absolutely congruent with the crystal of the mineral on which they are deposited, since the crystal elements are not identical. It is, therefore, of considerable interest to know what the exact orientation really is. Granted that the faces of contact lie in a plane, it still remains to determine which edges, if any, are parallel. The pair of substances chosen for the elucidation of this point was potassium perchlorate and barytes, for they exhibit the greatest difference of angle. Several fresh cleavage plates were immersed in hot saturated solutions of the former salt, which were allowed to cool slowly. The crystals were carefully dried, avoiding as far as possible any pressure which might slightly alter the orientation of the super-imposed crystals. Sometimes the crystals of potassium perchlorate were not dried by actual contact with filter-paper, but the latter was placed in contact with the barytes and the solution thus absorbed. The growths were measured on the two-circle goniometer, which is invaluable for such work.

Consider, first, the case of a crystal of potassium perchlorate growing on barytes with two prism faces in contact; then, if an edge $m:c$ of the one is parallel to an edge $M:C$ of the other, the edges $m:m$, $M:M$ must be parallel, since in both substances the angle $c:m$ is 90° . The angles between the planes of contact m and M , and the other faces, m_1 and M_1 , respectively, however, will not be the same, since $m:m_1$ and $M:M_1$ differ by $2^\circ 22'$.

The results obtained, although pointing to the above as the ideal position, showed slight variations therefrom. The angle between the faces of contact—which ideally should be 0° —was never greater than $20'$, and generally was a few minutes only. It was also found that

FIG. 6.



the edge $c:m$ is parallel to the edge $C:M$, and the angle $m_1:M_1$ always approximated to the theoretical angle $2^\circ 22'$.

Now consider the growths on the basal cleavages of barytes; granted that the contact-faces are parallel, the question arises whether an edge $c:m$ of the potassium perchlorate is parallel to an edge $C:M$ of the barytes, the other edge $c:m_1$ consequently making an angle of $2^\circ 22'$ with the edge $C:M_1$, or whether the crystallographic axes are parallel instead of these pairs of edges. Now, if the first alternative be correct, there is no reason why one pair of edges $C:M$, $c:m$ should be preferred to the other pair, and when several crystals of potassium perchlorate are grown on one crystal of barytes, there is no reason why the former, *inter se*, should be exactly congruent; if, however, the crystallographic axes be parallel, it follows necessarily that all the crystals of potassium perchlorate will be congruent.

The goniometrical results showed that the contact-faces were coplanar (subject to variations of a few minutes); they proved, too, that although the positions of various crystals on the same piece of barytes varied by $2\frac{1}{2}^\circ$, they yet tended to be such that either the edges $m : c$, $M : C$ or the edges $m_1 : c$, $M_1 : C$ were parallel. It will be seen from Fig. 6 that the position of crystal *B* can be derived from that of crystal *A* by a counter-clock-wise rotation of $2^\circ 22'$; rarely was a crystal orientated in a position derivable from that of *A* by a small clock-wise, or from that of *B* by a small counter-clock-wise, rotation, in which cases no prism edges would be parallel. Thus, so far as could be made out, it is the prism edges which are congruent. Now, parallel growths may be regarded as the result of the fitting together of two similar and almost identical structures; hence, it might follow that, in a parallel growth, those similar edges of the two substances would be absolutely congruent along which the crystal-units are most nearly equally spaced. The topic axes of potassium perchlorate and barytes are :

	χ .	ψ .	ω .	ξ .
KClO ₄	3.7360	4.7878	6.1307	3.0365
BaSO ₄	3.6509	4.7899	5.9472	3.0113
Difference ...	0.0851	-0.0021	0.1835	0.0252

Now the edges of the potassium perchlorate developed in contact with the barytes were $c : q$, $c : r$, and $c : m$, and the distances between contiguous crystal-units along these three directions are given by χ , ψ , and ξ respectively. Since the ψ -axes are almost identical, it would appear at first sight that the edges $c : r$ (the ψ -axes) should be parallel. But in this case (since the angle between the zones cr and cq is 90° in both substances) the edges $c : q$ would necessarily be parallel also: but these edges exhibit the greatest difference of spacing, and would not be expected to fit (compare the values of χ). On the other hand, the difference between the ξ -values is fairly small, and, moreover, the ξ -values themselves are the smallest; that is to say, the particles along the edge $c : m$ are the most densely packed, and also the most similar in the two crystals. This may account for the observed fact that a pair of edges $c : m$ is parallel.

(III) *Are Substances like Sodium Nitrate and Calcite, Barytes and Potassium Perchlorate, Isomorphous?*

The later definition of isomorphism by Mitscherlich was: "Substances possessing an analogous composition, which crystallise in the same form (or in similar forms), and which are capable of mixing in any proportions, are isomorphous"; but the terms of this definition are unsatisfactory for three reasons :

(1) Analogous chemical composition must be held to imply that dissimilar groups can replace each other, for example :

NaSi and CaAl in the feldspars.

CaSi and 2Al in the pyroxenes.

TiF₂, NbOF and WO₂ in the compounds described by Marignac.

(2) Similarity of form and angle are found with substances which probably differ in symmetry, for instance, KLiSO₄ and NaLiSO₄ ; NaCl and KCl.

(3) The formation of mixed crystals is not limited to substances of analogous composition, thus, ammonium chloride forms mixed crystals with ferrous chloride, ferric chloride, and manganic chloride ; further, the miscibility of some "isomorphous" substances is very limited indeed.

Now calcite and sodium nitrate possess certain similarities of chemical composition, in fact, they resemble each other in much the same way as do albite and anorthite, for example :

		Valencies.
{ Albite, NaAlSi ₃ O ₈	= NaSi(AlSi ₂ O ₃).	Na + Si = V. }
{ Anorthite, CaAl ₂ Si ₂ O ₈	= CaAl(AlSi ₂ O ₃).	Ca + Al = V. }
{ Sodium nitrate, NaNO ₃	= NaN(O ₃).	Na + N = VI. }
{ Calcite, CaCO ₃	= CaC(O ₃).	Ca + C = VI. }
{ Potassium perchlorate, KClO ₄	= KCl(O ₄).	K + Cl = VIII. }
{ Barytes, BaSO ₄	= BaS(O ₄).	Ba + S = VIII. }

They also possess similar forms and angles ; moreover, they exhibit the following physical properties :

Comparison of Physical Properties of Calcite and Sodium Nitrate.

		Calcite.	NaNO ₃ .	
Cleavage.		{100}	{100}	
$c : a$		0.8543	0.8276	
$r : r$		71°55'	73°30'	
Molecular volume		36.8	37.8	
Tropic axis ($\chi = \psi = \omega$)		4.0478	4.1276	
Optical properties:—				
	Birefringence.	Negative.	Difference.	Negative.
Refractive indices...	ω	B 1.6531	0.074	1.579
		D 1.6585	0.071	1.587
		E 1.6636	0.070	1.594
		H 1.6833	0.057	1.626
Refractive indices...	ϵ	B 1.4839	0.149	1.335
		D 1.4863	0.150	1.336
		E 1.4887	0.142	1.337
		H 1.4978	0.154	1.344
	$(\omega - \epsilon)$	B 0.1692	—	0.244
	$(\omega - \epsilon)$	H 0.1855	—	0.282
Induced magnetism.		Diamagnetic.	Diamagnetic.	
Magnetic character.		Positive.	Positive.	
Artificial twinning: twin pl.		{110}	{110}	
Thermal conductivity (Jannettaz).		Greater axis of ellipsoid parallel to principal axis.		

In view of the above remarkable resemblances, the question arises whether calcite and sodium nitrate should not be called isomorphous, in spite of the fact that they do not form mixed crystals.

Now there are two other properties which have been long advanced as characteristic of isomorphous substances: (1) the formation of parallel growths, (2) the relief of supersaturation of a solution by a crystal of a substance isomorphous with the solute. It has been shown that the first property is possessed by calcite and sodium nitrate; further, Professor Miers and M. Chevalier have found that calcite does relieve supersaturation in a metastable solution of sodium nitrate, and this the present author has confirmed.

The parallel growth of sodium nitrate and calcite has long been known, and it has led many mineralogists, especially Tschermak, to entertain the view that the two substances are isomorphous; yet little significance has been attributed to it by many others, partly because the case was regarded as unique. The views of Groth and Retgers may be given here, since they were most prominent in denying the isomorphism. Groth says, "Zweierlei Molecüle von sehr verschiedener Moleculargrösse können wohl, jeder Art für sich, zu einen Aufbau von übereinstimmender Struktur sich vereinigen, aber niemals können sie mit einander gemischt einen homogenen Krystall liefern. Hierin dürfte wohl die einfache Erklärung für die Tatsache liegen, das gewisse chemisch nicht analoge Körper, welche sehr ähnliche Krystallstruktur besitzen, wie Natronsalpeter und Kalkspath, zwar im Stande sind, der eine auf den Krystallen des anderen als regelmässige Fortwachsung zu krystallisieren, niemals aber isomorphe Mischungen zu liefern."

It may be pointed out that, although of different molecular weight, calcite and sodium nitrate are really not of different molecular size, for their molecular volumes are almost identical.

Retgers asserted that parallel growth may not be taken as a criterion for isomorphism. He says of parallel growth: "Das Phänomen ist nicht beschränkt auf isomorphe, sondern erstreckt sich auch auf morphotrope Körper. . . . Die ganze Erscheinung hat also nicht den geringsten Werth für chemische Schlussfolgerungen. Es ist weiter nichts als ein Influenciren auf die Richtung bei der Ausscheidung aus dem flüssigen in den festen Zustand und sehr gut vergleichbar dem sich parallel Orientiren von Eisenstäbchen in der Nähe eines starken Magnetes." Now Retgers here confused the two terms, parallel and regular growths: although it is true that regular growths of morphotropic substances (or of substances which are apparently not even morphotropic) are known, yet parallel growths as exhibited by calcite and sodium nitrate, potassium perchlorate and barytes—that is, where the substances are isostructural and the whole orientation is congruent

—such parallel growths are not found among morphotropic substances (the feldspars being held to be isomorphous). Further, there is only a superficial analogy between parallel growths and the action of a magnet on iron-filings; because, although the magnet does orientate the filings in a definite manner, yet the position taken up by the molecules or the crystal-units of the filings is not, necessarily, congruent with the position of the molecules of the orientator—the magnet.

Retgers has proposed another definition of isomorphism: “Two substances are really only isomorphous when the physical properties of their mixed crystals are continuous functions of the chemical composition.” If this definition be accepted, substances which do not, or cannot, form mixed crystals are rigidly excluded; moreover, complete investigations of the physical properties of mixed crystals have been made very seldom. Retgers, however, was not consistent, for, in ridiculing a proposal (made by Arzruni) that a similar degree of solubility may be taken as characteristic of isomorphous compounds, he said “ CaF_2 and CaCl_2 are both cubic, the former being nearly insoluble, the latter extraordinarily deliquescent. Mixed crystals, therefore, cannot be formed from an aqueous solution; yet the two compounds are isomorphous. It is possible that a common solvent might exist, from which mixed crystals would be obtainable; or the latter might be obtained from the fused mixture.” No mixed crystals, no parallel growths, no relief of supersaturation had been observed; therefore the only reason for asserting that these two substances are isomorphous was that both are cubic, coupled with the fact that chlorine and fluorine sometimes replace each other isomorphously. The remarks of Retgers concerning calcium chloride and calcium fluoride are really applicable to sodium nitrate and calcium carbonate.

It has been shown above that in an isostructural series the formation of parallel growths depends on a similarity of molecular volume. The question arises whether the miscibility of isomorphous salts also depends on this, but an examination of the investigated cases, especially of those with limited miscibility, has failed to lead to the recognition of the existence of any connection between molecular volume and miscibility.

In spite of this difference, however, the author does not see why the parallel growths should not be taken as evidence in favour of isomorphism in lieu of the formation of mixed crystals. It may be concluded, then, that the isostructural substances, sodium nitrate and calcite, are really isomorphous.

Reliable results would probably not be obtainable from experiments on the relief of supersaturation of potassium perchlorate or permanganate by barytes, celestine, or anglesite; in the former case, owing to the slight solubility of the salt, in the latter because of the opacity

of the solution. But the analogies which have been made out, for example, composition, form, angle, molecular volume, and the formation of parallel growths, point to the isomorphism of these substances.

The author hopes to make an investigation of the physical properties of the perchlorates and permanganates, in order to see whether the two groups, calcium carbonate—sodium nitrate, potassium perchlorate—barium sulphate, are completely analogous.

(IV) *Other Experiments with Solutions on Minerals.*

Growths on Mica.

In the course of the present investigation, the author also studied the growths on mica, first obtained by Frankenheim, whose results were, in general, confirmed, and the following additional interesting facts were observed. In the case of potassium iodide, part came down in cubes which were totally irregular (Frankenheim asserted that they are regular); besides these, skeletal, triangular-shaped masses—often twinned—were present and were regularly arranged, one side of the triangle being parallel to the plane of symmetry of the mica. Potassium bromide gave similar results, but here in some rare cases cubes standing on a face $\{111\}$ were observed, and they possessed the same orientation as the triangles. Potassium chloride gave skeletal growths which were quite irregular. Sodium bromide and iodide crystallise in monoclinic forms containing two molecules of water of crystallisation; the deposition is irregular. Finally, sodium chloride gave irregularly orientated cubes. Sodium nitrate generally comes down in rhombohedra which have no definite orientation; sometimes, however, triangular-shaped masses are met with, which possess the same orientation as the above salts. Moreover, rhombohedra standing on $\{\bar{1}\bar{1}\bar{1}\}$ have been obtained in the same orientation as the triangular crystals; rarely is the face $\{111\}$ developed, and it is always pitted, and generally disappears on the further growth of the crystal. In some cases a negative rhombohedron was observed.

The above regular growths do not meet with so ready an explanation as the isostructural substances previously studied, for the molecular volume of the mica is certainly far greater than those of the substances deposited. It is worthy of remark, however, that the structure of the haloid compounds may not be greatly different from that of sodium nitrate, for the cleavage is very similar. Further, the orientation of the regularly deposited crystals of all the above substances was the same, as were also the forms. Is it merely a coincidence that the above crystals were so orientated that a trigonal axis is parallel to the pseudo-trigonal axis of the mica?

Since mica causes substances so diverse as the above to crystallise

on it in regular position, it was resolved to study the crystallisation of other salts on mica and on other minerals possessing good cleavages.

Potassium nitrate gave three kinds of crystals on mica:

(1) Ordinary orthorhombic prisms which were irregular,

(2) Equilateral-triangular, and

(3) Skeletal-hexagonal masses, which were both orientated in the same regular manner as the crystals of potassium iodide.

Attempts to detach these crystals in order to investigate their optical properties were without success owing to their extreme tenuity. Crystallisation on the thinnest piece of mica obtainable by cleavage was also tried, but the interference figure of the mica was still predominant. The triangular- and hexagonal-crystals with the above orientation remained dark when the nicols were rotated, but a few crystals not in the above orientation polarised in bright colours, and are therefore strongly birefringent.

Potassium nitrate, crystallised on glass, gave the orthorhombic crystals only.

Hydroquinone on Calcite.

It was found that two kinds of crystals of hydroquinone are deposited on calcite from a warm aqueous solution: (1) long prisms irregularly arranged, and (2) stouter plates which were orientated regularly with one side parallel to the longer diagonal of the calcite-rhomb. The extinction of the prism-modification is straight and the birefringence weak; this is, therefore, probably the hexagonal modification (hydroquinone is dimorphous); they were too small to be measured, but crystals of a similar habit obtained in a test-tube were, on measurement, found to be hexagonal.

The second regularly-orientated modification was also obtained by allowing a solution to crystallise on glass, and was found to be strongly birefringent; the quartz wedge compensates across the prism, and examination in convergent polarised light shows the first mean line is normal to the section. The axial angle is very wide and the plane of the optic axes is parallel to the direction of compensation; hence the birefringence is positive. The extinction is straight. This modification may be the monoclinic one.

Experiments with other Minerals and Salts.

The majority of the experiments made with other minerals and salts gave negative results, so the details of each case are not gone into; the following is a list of the substances tried which all gave irregularly orientated deposits. Only fresh cleavage surfaces of the mineral were used.

Calcite.—Potassium iodide, bromide, and chloride.

Mica.—Ammonium alum, barium nitrate, ammonium nitrate, potassium fluoride and perchlorate, and sodium chlorate.

Gypsum.—Sodium nitrate (Frankenheim says regular); potassium chromate, iodide, perchlorate, and permanganate; sodium chloride and barium nitrate.

Rock Salt.—Potassium bromate, chromate, perchlorate, and sulphate; sodium chlorate.

Barytes.—Potassium chromate, nitrate, and sulphate.

Cubic Substances on Cubic Minerals.

The following failed to yield regular growths :

On blende, $V = 23.75$.

	<i>V</i> .
Ammonium alum	552.2
Barium nitrate	81.0
Lead nitrate	73.3
Sodium chloride	27.2
Potassium chloride.....	37.4
Sodium chlorate	46.5
Sodium bromate	45.2
Potassium iodide	53.24
Potassium cyanide	?

	<i>V</i> .
On fluor-spar	24.5

All the above salts, and also ammonium chloride and silver chloride (from ammoniacal solution), failed to give any regular growths on fluor-spar.

The Aragonite Group.

It has been asserted by v. Hauer (*Sitzungsber. K. Akad. Wien.*, 1860, 39, 612) that de Senarmont obtained an overgrowth, in parallel position, of potassium nitrate on aragonite; but neither Arzruni nor the author has been able to find an account of this in de Senarmont's published papers.

It was decided to investigate this point, since the crystallographic relationships of potassium nitrate and aragonite are much the same as those of calcite and sodium nitrate. Crystals of aragonite, from Bilin, possessing bright faces, were cleansed by means of a saturated solution of potassium nitrate, and the two methods previously used—the drop and the cooling method—were applied in the attempt to obtain regular depositions; but no trace of regularity could be found

in the crystals of potassium nitrate deposited. Cleavage faces, too, were tried, but all to no purpose. Crystals of cerussite, exhibiting the forms $m\{-110\}$, $v\{-120\}$, $q\{-011\}$, $\{021\}$, and $\{010\}$ were also tried; but here, again, no regular growths were obtained. Twin-crystals of witherite (the only ones available) with very rough faces also afforded no regular growths.

(V) *Parallel Growths of Isomorphous Salts on each other.*

Investigations were then made in order to find whether similarity of molecular volume is as necessary for the formation on each other of parallel growths in the case of isomorphous salts which do form mixed crystals as is apparently the case with substances like potassium perchlorate and barytes, which do not; for, if isomorphous salts were found capable of giving parallel growths, no matter how great the difference of molecular volume, this property would distinguish them from merely isostructural substances. It has, of course, long been known that isomorphous substances are capable of giving zone-crystals, but this property has, hitherto, not been systematically studied, and the simple drop method does not seem to have been used in its investigation. In order to test this point, the series of isomorphous salts selected should show great differences of molecular volume amongst its members, and this condition is most likely to be fulfilled in groups containing isomorphously replaceable acidic—as well as basic—radicles. The only such groups which have been worked out with regard to volume properties, as well as geometrical, are:

- (1) Sulphates and selenates of the alkalis (Tutton),
- (2) Double sulphates and selenates of the form $R_2SO_4 \cdot MSO_4 \cdot 6H_2O$ (Tutton),
- (3) The alums (Pettersson),
- (4) The haloid salts of the alkalis (Sprockhoff), and
- (5) The permanganates and the perchlorates of the alkalis.

Parallel Growths of the Perchlorates and Permanganates on each other.

Freshly-prepared basal and prismatic cleavage-pieces of the salts were used, and drops of a saturated solution of another salt were placed on them and the crystallisation watched. The rapidity with which crystals appeared on the mother-crystal varied with the individual pairs of salts. The growths always appeared more quickly, however, than with calcite and sodium nitrate; in some cases they appeared as soon as the drop touched the crystal. All possible pairs of substances were not taken, but all the salts were used, either as crystals or in solution, and all gave parallel growths. This is no

doubt to be accounted for by the fact that, as shown on p. 1135, they do not differ greatly in molecular volume.

Following is a list of the experiments :

KMnO ₄ aq.	on crystals of	KClO ₄ , RbClO ₄ , and CsClO ₄ .
RbMnO ₄ aq.	„	KClO ₄ .
AmClO ₄ aq.	„	KClO ₄ .
TlClO ₄ aq.	„	KClO ₄ .
KClO ₄ aq.	„	CsClO ₄ .
CsMnO ₄ aq.	„	KClO ₄ .

Cesium permanganate is very slightly soluble in water, so the crystals deposited on a crystal of potassium perchlorate were extremely small ; there was no doubt, however, concerning the regularity of the deposition. Since cesium and potassium perchlorates possess, respectively, the highest and lowest molecular volumes of all the salts in the series, and since all the other pairs tried gave parallel growths, it is very probable that all possible pairs would also give parallel growths.

The results go far to prove that there is no inherent difference between the salts which form parallel growths on barytes, potassium perchlorate and permanganate, on the one hand, and those which do not, on the other ; moreover, they confirm the view that only a too great dissimilarity of molecular volume renders parallel growths impossible.

The investigation of the halogen salts of the alkalis is now in progress.

Growth of Two Salts possessing almost identical Molecular Volumes.

It was observed in the course of the above work that a drop of solution of a salt, placed on a crystal of the solute itself, does not on evaporation give rise to visible parallel crystals, but a few irregularly orientated crystals are formed ; a closer study showed, however, that the crystals which are formed really fall from the surface of the drop and are not formed in contact with the large crystal. Further, very often separate crystals are not formed at all, but the large crystal grows as a whole.

The examination of several pairs of isomorphous salts, selected at random, finally disclosed the fact that a drop of sodium bromate solution behaves in exactly the same manner when placed on a crystal of sodium chlorate—the solution evaporates without the formation of separate crystals. Now the molecular volumes of these two salts are almost identical, namely, 45·2 and 46·5 respectively. It therefore appeared likely that the property might be common to all pairs of isomorphous salts which possess nearly identical molecular volumes.

The crystallisation of various alums on each other, and of a solution of zinc sulphate on crystals of the less soluble magnesium sulphate, was studied. The molecular volumes of the latter salts are, respectively, 146.72 and 147.096, and the topic axes calculated from Dufet's measurements are :

	χ .	ψ .	ω .
ZnSO ₄ 7 aq.	6.28650	6.41955	3.63561
MgSO ₄ 7 aq.	6.31895	6.38361	3.64661
Differences	0.03245	0.03594	0.01100

In most cases no separate crystals were formed, but the solution evaporates, leaving a zonal growth of ZnSO₄, 7aq. on MgSO₄, 7aq.

The same behaviour has been found with solutions of chrome and ammonium alum on crystals of potassium alum, and with a solution of ammonium alum on crystals of chrome alum. Sometimes a few crystals were formed, but they were never parallel.

The molecular volumes of these alums are :

Chrome alum.....	542.2	} Otto Petterssen.
Potassium alum	541.6	
Ammonium alum	552.2	

There is therefore apparently a remarkable connection between the character of parallel growths and the amount of the difference of molecular volumes.

It is significant that the most beautiful examples of zonal-growths (Schichtkrystalle) recorded have been obtained from pairs of salts possessing almost identical molecular volumes; for example, by the immersion of crystals of zinc sulphate, nickel sulphate, or cobalt sulphate in a solution of magnesium sulphate; or, again, the various alums on each other (described by von Hauer). An explanation of the common occurrence of zonal structure in the feldspars may be found in the extraordinary similarity of molecular volume of the individual members of the group. The molecular volumes of the two extreme members, albite and anorthite, are respectively 100.13 and 101.49.

Complications which ensue owing to the Common Solubility of Two Salts in the same Solvent.

The deposition of a salt on crystals of an isomorphous salt which is soluble in the solution of the former is not a simple process due to evaporation alone; this follows from the observation that even if the solution of the former is not quite "saturated," crystals are still immediately deposited on the isomorphous salt. Further, on placing a

small fragment of the solute in the solution, it begins to dissolve, although apparently the same substance is simultaneously separating out on the crystal of the isomorphous salt. Again, if the solution (not saturated) is of a suitable concentration, a crystal of an isomorphous salt, when introduced, becomes covered with small crystals (generally in parallel position), but itself begins to dissolve; if the crystals introduced be very small and more soluble than the solute, it dissolves completely, and then the crystals of the solute, which have separated out, begin to dissolve themselves, and may totally disappear.

Suitable solutions of ammonium chloride, potassium iodide, and potassium chloride were prepared by slightly diluting the saturated solutions, and small cleavage-pieces of rock salt were pushed into drops of them; in all cases, crystals appeared on the rock salt, and the latter began to dissolve. Further, on adding a small crystal of the solute to the drop, it also began to dissolve; if, however, this crystal was placed on the rock salt, it did not dissolve. This shows that the concentration and composition of the solution vary greatly in different parts of the drop; the solution in contact with the rock salt is saturated with regard to the solute, whereas the rest of the solution is unsaturated. Crystals of ammonium perchlorate behave in the same way when immersed in a nearly saturated solution of thallium perchlorate. In the case of suitably diluted solutions of potassium bromide and potassium iodide, rock salt causes an immediate liberation of cubes in parallel position, whilst the rock salt itself dissolves away; finally, the cubes of potassium bromide and iodide dissolve.

Crystals of caesium chloride on immersion in potassium iodide solution dissolved rapidly, but in a remarkable manner; the sides of the crystals alternately grew and dissolved several times, until finally all had disappeared. Similarly, crystals of ammonium perchlorate cause a liberation of crystals of potassium perchlorate (in parallel position) from a nearly saturated solution of the latter salt, but dissolve rapidly themselves; finally, the crystals of potassium perchlorate themselves disappear.

We have seen that crystals of sodium chloride cause an immediate liberation of crystals of potassium iodide from a solution of the latter; now a crystal of potassium iodide also liberates crystals of sodium chloride from its aqueous solution, and if the solution of the latter be not quite saturated, the crystals of sodium chloride which have separated on the crystal of potassium iodide dissolve again completely after the solution of the potassium iodide.

The liberation of crystals of the solute in all the above cases is probably preceded by the dissolution of a small portion of the crystal of the isomorphous salt; this follows from a consideration of the fact that the solution was in many cases not saturated in the absence of the crystal

introduced. This, together with the variations of concentration which it causes in different parts of the solution, is sufficient to explain the above observations. It follows from Roozeboom's thermodynamic deduction of the laws of equilibrium between isomorphous salts and a common solvent that a salt cannot be in equilibrium with a pure saturated solution of another salt; an interchange of salt and solute will take place in general, with the formation of mixed crystals. Now it is extremely unlikely that the mixed crystals first formed will have the same composition as the mixed crystals which are finally in equilibrium with the solution, for the equilibrium is only gradually reached and not *per saltum*; the composition of the solution, therefore, is continually changing, and mixed crystals of varying concentrations will be formed during the process, which will all in turn dissolve again. The best example of this phenomenon noticed by the author was found with crystals of caesium chloride and a solution of potassium iodide. It follows from the above considerations that the crystals deposited on a crystal of an isomorphous salt are not pure crystals of the solute, but mixed crystals; nevertheless, the percentage of the solute will be very high, and hence the molecular volume of the mixed crystals deposited will not be greatly different from the molecular volume of the pure solute.

Summary of Conclusions.

(1) The parallel deposition of sodium nitrate on fresh cleavage surfaces of calcite is independent of the habit or variety of the latter, so long as a good cleavage surface is obtainable.

(2) Isomorphous mixtures of sodium and silver nitrate, and sodium and potassium nitrate, behave like pure sodium nitrate.

(3) An essential condition for parallel growths is a clean surface: in the experiments described, contact with the unimpaired crystalline material was found to be absolutely necessary.

(4) Artificial twinning over the glide-plane, σ -{110}, does not prevent the parallel deposition of crystals.

(5) The orientation of the crystals deposited is not affected by crystallisation in a magnetic field.

(6) Sodium nitrate is deposited in regular position on certain other forms of calcite besides the cleavage surface; in all cases congruent edges of the calcite and sodium nitrate are parallel.

(7) Sodium nitrate does not form parallel growths on the other minerals of the calcite group—chalybite, calamine, dolomite, rhodochrosite, breunnerite, and diallogite—nor on barytocalcite.

(8) The necessary condition for parallel (and regular) growth is

closeness of molecular volume rather than similarity of angle (or of axial ratios).

(9) Parallel growths have been discovered amongst the members of another, and far more numerous, group of isostructural minerals and salts. Potassium perchlorate and potassium permanganate form parallel growths on the minerals, barytes, anglesite, and celestine, whereas the perchlorates of rubidium, cesium, ammonium, and thallium, and the permanganates of rubidium, cesium, and ammonium, do not. Here, again, closeness of molecular volume—and, hence, of topic axes—is necessary for parallel growth.

(10) The above isomorphous salts do not form parallel growths on anhydrite; the latter is, however, not isostructural with the former, for it has a different cleavage.

(11) The parallel growths and, in addition, the extraordinary similarities—crystallographic and physical—of sodium nitrate and calcite (and also of potassium perchlorate and barytes, &c.), is strong evidence for regarding them as isomorphous. This view is in harmony with the observations regarding the action of calcite on a metastable solution of sodium nitrate.

(12) Regular growths of potassium bromide, potassium iodide, sodium, and potassium nitrate can be obtained on mica; also of hydroquinone on calcite.

(13) No parallel growths of cubic salts on cubic minerals were obtained.

(14) No parallel growths were obtained in the potassium nitrate-aragonite group.

(15) All the members of the perchlorate-permanganate group form parallel growths on each other; this is the first investigation of the parallel growths of substances which form mixed crystals.

(16) Pairs of isomorphous salts, the molecular volumes of which are almost identical, form zonal-growths (*Schichtkrystalle*) rather than parallel growths of distinct crystals.

(17) The perchlorates of potassium, rubidium, cesium, ammonium, and thallium, and the permanganates of the first four metals, form an isomorphous group. The crystallographic relationship between the perchlorates and permanganates is the same as that between the sulphates and selenates; the crystallographic evidence for placing manganese in the seventh group of the periodic classification is therefore the same as holds for placing selenium in the sixth group.

I take this opportunity of expressing my thanks to the Chemical Society for defraying the expenses of this research by means of a grant.

In conclusion I desire to record my thanks and gratitude to Professor

H. A. Miers, who not only proposed the above research to me, but also continuously supported me with happy suggestion and helpful criticism.

MINERALOGICAL DEPARTMENT,
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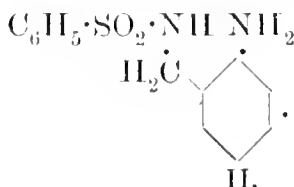
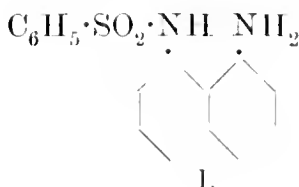
CXV.—*The Diazo-derivatives of the Mixed Aliphatic Aromatic ω -Benzenesulphonylaminobenzylamines.*

By GILBERT THOMAS MORGAN and FRANCES MARY GORE
MICKLETHWAIT.

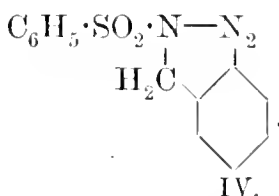
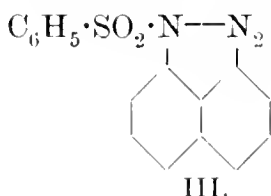
THE acylsulphonyl derivatives of the purely aromatic ortho- and para-diamines give rise to two characteristic series of diazo-anhydrides. The compounds of the ortho-series are very stable substances produced even in the presence of mineral acids and not hydrolysed by hot acids or alkalis. The para-diazoimides, on the other hand, are formed only when the mineral acid present is replaced by a weaker organic acid, and the change is readily reversed by treating the diazo-anhydride with cold concentrated hydrochloric acid. The para-diazoimides are further characterised by their colour, all the members of the series hitherto prepared being distinctly yellow (Trans., 1905, 87, 73, 921, 1302). In the ortho-series, the appearance of colour is exceptional, and the acyl-*o*-diazoimides are generally described as being colourless substances.

In their last communication on this subject (this vol., p. 4), the authors described benzenesulphonyl-1:8-naphthylenediazoimide and showed that this heteronuclear peri-derivative was similar in all respects to the para-diazoimides. As these facts indicated that the production of a coloured diazoimide occurs even when the aminic nitrogens are situated in different aromatic rings, it seemed of interest to ascertain whether similar compounds would be formed from mixed aliphatic aromatic diamines containing the acylamino-group in an open chain. Accordingly, the ω -benzenesulphonyl derivatives of the three aminobenzylamines were examined from this point of view, and the results obtained are recorded below.

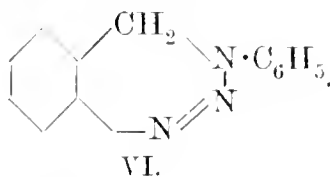
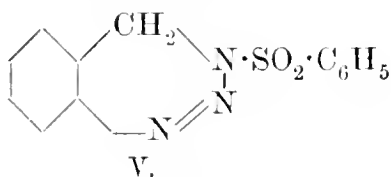
The structural relationship between ω -benzenesulphonyl-*o*-aminobenzylamine (II) and benzenesulphonyl-1:8-naphthylenediamine (I) is indicated by the following formulæ:



The two bases behave similarly when their hydrochlorides are treated with nitrous acid; they both yield soluble diazonium salts which do not undergo condensation in the presence of excess of the mineral acid, and in each case the addition of excess of sodium acetate to the acid solution determines the formation of a diazoimide, but whereas the peri-diazoimide (III) is yellow, the new ω-benzenesulphonyl-o-benzylenediazoimide (IV) is colourless.

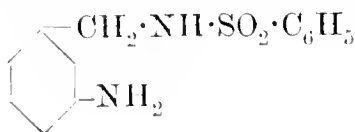


In other respects the two compounds are similar, both undergo fission on treatment with cold concentrated hydrochloric acid, regenerating the original diazonium chlorides. In spite of its lack of colour, there seems no reason to doubt that the new mixed diazoimide is a diazo-compound and not a diazonium derivative, and accordingly it may be represented by the more expanded formula V, this view of its constitution agreeing with the configuration ascribed to the analogous colourless β-phenylphenylenedihydrotriazine (VI) obtained by M. Busch from o-aminobenzylaniline (*Ber.*, 1892, 25, 448).

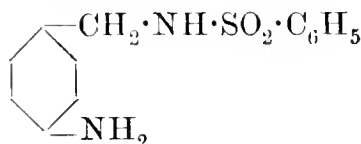


In the case of ω-benzenesulphonyl m-aminobenzylamine (VII), it was found that the tendency to form a diazo-anhydride had greatly diminished. The diazonium chloride of this base is not appreciably affected by excess of aqueous sodium acetate, but when the solution is treated with excess of potassium hydrogen carbonate a pale yellow precipitate slowly separates. The yield of this compound is, however, somewhat small, representing only about 10 per cent. of the diamine employed. The remainder of the diazo-compound remained uncondensed, and was recognised by combining it with β-naphthol in alkaline solution. This formation of diazo-anhydride, which is therefore very incomplete, differs markedly from the reaction taking place with ω-benzenesulphonyl-o-aminobenzylamine, where the condensation is quantitative.

o-Benzenesulphonyl-*p*-aminobenzylamine (VIII), when subjected to the action of nitrous acid under similar conditions, furnishes a diazonium chloride, which does not undergo condensation on treatment with aqueous sodium acetate or potassium hydrogen carbonate, the solution, after the addition of these reagents, still yielding the calculated amount of azo- β -naphthol derivative.

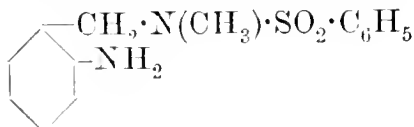


VII.

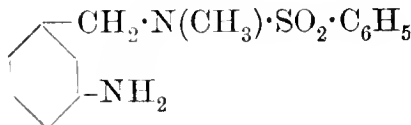


VIII.

In the two cases where condensation had occurred, the reaction was shown to depend on the presence of the hydrogen atom of the benzenesulphonylamino-group ($\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$), for when this was replaced by methyl, no formation of insoluble diazoimide took place:



IX.



X.

o-Benzenesulphonyl-*o*-methyl-*o*-aminobenzylamine (IX) and its meta-isomeride (X) are both readily diazotised to soluble diazonium chlorides, which are not affected by aqueous alkali acetates or bicarbonates and yield insoluble, red azo- β -naphthol derivatives.

EXPERIMENTAL.*

The three phthalalnitrobenzylimides,



required in this research were obtained by condensing potassium phthalimide with *o*-, *m*-, and *p*-nitrobenzyl chlorides in the manner indicated by Gabriel (*Ber.*, 1887, 20, 2227). The hydrolysis of the three substituted imides was most effectively carried out by Wolff's method (*Ber.*, 1892, 25, 3031), in which an intimate mixture of the imide with concentrated acetic and hydrochloric acids is heated under pressure at 180° for three to five hours. Equal parts by weight of the two acids were employed, and about seven parts of this mixture were used for three parts of the imide. In this way, the hydrochlorides of the three nitrobenzylamines were obtained and converted into their benzenesulphonyl derivatives by the Schotten-Baumann reaction. The main product of the reaction consists of the mono-benzenesulphonyl

* The authors' thanks are due to Mr. A. E. Dawe for much valuable assistance in the preliminary experiments of this investigation.

derivative, providing that only a slight excess of benzenesulphonic chloride is employed; with larger proportions of this reagent, a certain amount of the disulphonyl compound is formed. The crude benzenesulphonyl derivatives were dissolved in aqueous caustic alkalis, reprecipitated with dilute acetic acid, and recrystallised from alcohol or benzene.

Benzenesulphonyl-o-nitrobenzylamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$, separated from benzene in well-defined, hard, amber-yellow, prismatic crystals melting at 92° .

0.3568 gave 30 c.c. nitrogen at 18° and 755 mm. $\text{N} = 9.65$.

$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 9.58$ per cent.

Benzenesulphonyl-m-nitrobenzylamine crystallised readily from benzene in colourless needles or pale yellow prisms and melted at $123\text{--}124^\circ$.

0.3627 gave 32.7 c.c. nitrogen at 19° and 768 mm. $\text{N} = 10.28$.

0.1855 „ 0.1554 BaSO_4 . $\text{S} = 11.50$.

$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 9.58$; $\text{S} = 10.97$ per cent.

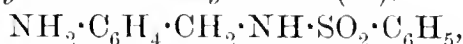
Benzenesulphonyl-p-nitrobenzylamine crystallised from benzene in lustrous, light orange leaflets melting at 118° .

0.2284 gave 19.4 c.c. nitrogen at 23° and 759 mm. $\text{N} = 9.57$.

Reduction of the Benzenesulphonylnitrobenzylamines.

The foregoing benzenesulphonylnitrobenzylamines were readily reduced by iron filings and dilute acetic acid.

ω -Benzenesulphonyl-o-aminobenzylamine (II),



was obtained by reducing 5 grams of the corresponding nitro-compound with 10 grams of iron, 5 c.c. of glacial acetic acid, and 100 c.c. of hot water. After boiling for one hour, the mixture was rendered alkaline with 5 grams of sodium carbonate and filtered, when a small portion of the diamine separated from the aqueous solution as a white powder; the greater part was extracted by alcohol from the residue and crystallised from dilute alcohol in well-defined, colourless, elongated plates melting at $108\text{--}110^\circ$.

0.2462 gave 23.0 c.c. nitrogen at 20° and 767 mm. $\text{N} = 10.76$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 10.68$ per cent.

This substance crystallises from benzene in colourless plates melting at 95° and containing solvent of crystallisation.

0.1964 gave 14.1 c.c. nitrogen at 18° and 758 mm. $\text{N} = 8.27$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\text{S} \cdot \text{C}_6\text{H}_6$ requires $\text{N} = 8.23$ per cent.

This specimen, when crystallised from dilute alcohol, lost its benzene and separated in lustrous, colourless leaflets having the composition $C_{13}H_{14}O_2N_2S$ and melting at 109° .

ω-Benzenesulphonyl-*m*-aminobenzylamine (VII) was prepared by treating 4 grams of the nitro-compound with 8 grams of iron, 4 c.c. of glacial acetic acid, and 150 c.c. of water. After boiling for thirty minutes, 4 grams of sodium carbonate were added, the mixture was then filtered, the residue extracted with alcohol, the combined filtrates evaporated nearly to dryness, and the final residue dissolved in 50 per cent. acetic acid, from which solution the diamine was deposited as a pale yellow solid (m. p. $85-87^\circ$) on the addition of ammonia. When crystallised either from benzene or very dilute alcohol, this base separated in yellow, tabular crystals having a resinous appearance, which contained solvent of crystallisation and melted at $76-78^\circ$. When kept in a desiccator over sulphuric acid or when heated in the steam-oven, these crystals lost their combined solvent and also their lustre, becoming appreciably viscous; finally, they hardened again and then melted indefinitely at $80-85^\circ$.

0.3198 gave 29.3 c.c. nitrogen at 19.5° and 766 mm. $N = 10.59$.

$C_{13}H_{14}O_2N_2S$ requires $N = 10.68$ per cent.

ω-Benzenesulphonyl-*p*-aminobenzylamine (VIII) was obtained when 4 grams of nitro-compound, 8 grams of iron filings, 4 c.c. of glacial acetic acid, and 100 c.c. of water were boiled for forty minutes, the remainder of the preparation being carried out as in the case of the ortho-isomeride. The base, when crystallised from benzene, separated in colourless needles melting at $131-133^\circ$.

0.1180 gave 11.1 c.c. nitrogen at 19° and 768 mm. $N = 10.93$.

0.1808 „ 0.1671 $BaSO_4$. $S = 12.68$.

$C_{13}H_{14}O_2N_2S$ requires $N = 10.68$; $S = 12.21$ per cent.

Action of Nitrous Acid on the ω-Benzenesulphonyl-aminobenzylamines.

Benzenesulphonyl-o-benzylendiazoimide, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{N}:\text{N} \end{smallmatrix} \text{N} \cdot \text{SO}_2 \cdot C_6H_5$.

One gram of *ω*-benzenesulphonyl-*o*-aminobenzylamine was diazotised with 9 c.c. of concentrated hydrochloric acid and 2 c.c. of 20 per cent. aqueous sodium nitrite; 3 grams of ice were added during the process and the mixture was cooled externally with ice and salt. A colourless solution of diazonium chloride was obtained, which remained perfectly clear on dilution and yielded the colourless diazoimide on the addition of excess of aqueous sodium acetate. The precipitate consisted of minute, colourless leaflets; the filtrate gave no coloration with

alkaline β naphthol, showing that the condensation was complete. This diazoimide decomposed violently at about 130°.

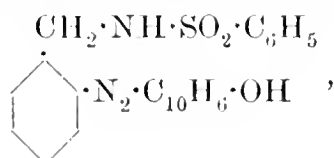
0.2650 gave 0.5569 CO₂ and 0.1070 H₂O. C = 57.31 ; H = 4.49.

0.2509 „ 33.7 c.c. nitrogen at 19.5° and 767 mm. N = 15.56.

0.2370 „ 0.2090 BaSO₄. S = 12.11.

C₁₃H₁₁O₂N₃S requires C = 57.10 ; H = 4.03 ; N = 15.38 ; S = 11.72 per cent.

The diazeimide when treated in the cold with a mixture of concentrated hydrochloric and acetic acids dissolved, leaving only a slight viscid, brown residue; the solution, when diluted considerably and poured into alkaline β-naphthol, yielded at once a light red, granular precipitate of *benzenesulphonyl-ω-aminotoluene-2-azo-β-naphthol*,



which, when crystallised from benzene, separated as a bright scarlet, microcrystalline powder melting at 161–163°.

0.1860 gave 16.0 c.c. nitrogen at 20° and 769 mm. N = 9.96.

C₂₃H₁₉O₃N₃S requires N = 10.07 per cent.

This azo-derivative was also prepared directly from the diazonium chloride of ω-benzenesulphonyl-*o*-aminobenzylamine.

Benzenesulphonyl-m-benzylenediazoimide.

ω-Benzenesulphonyl-*m*-aminobenzylamine was diazotised in hydrochloric acid solution according to the method adopted in the case of the ortho-base. The pale yellow solution thus obtained, which contained only a slight brown turbidity, was diluted considerably, filtered, and treated with excess of aqueous sodium acetate. The solution then became slightly turbid, but no further change occurred until excess of potassium hydrogen carbonate was added, when an amorphous, pale yellow precipitate slowly separated, and was collected after three hours, washed successively with water, alcohol, and light petroleum, and finally dried in the desiccator; 4 grams of the meta-base yielded 0.6 gram of the diazoimide. The compound could not be obtained crystalline, as it decomposed on warming with solvents.

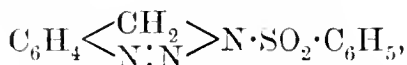
0.2192 gave 0.4538 CO₂ and 0.0838 H₂O. C = 56.46 ; H = 4.25.

0.1144 „ 14.2 c.c. nitrogen at 20° and 764 mm. N = 14.29.

0.1131 „ 0.0979 BaSO₄. S = 11.88.

C₁₃H₁₁O₂N₃S requires C = 57.14 ; H = 4.03 ; N = 15.38 ; S = 11.72 per cent.

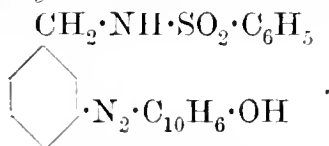
These data indicate that the substance has the composition of a diazoimide. It is insoluble in aqueous alkalis or acids, and is decomposed by the concentrated mineral acids (30 per cent. HCl or 50 per cent. H_2SO_4) even in the cold, evolving two-thirds of its nitrogen, and leaving a dark brown, resinous product. When this experiment was performed in the volumeter with cold sulphuric acid, 9.5 per cent. of nitrogen was eliminated, the calculated value for



namely, two-thirds of the total amount, being 10.24. This compound differs so much from the well-defined, crystalline ortho-diazoimide (p. 1162), and also from the aromatic para-diazoimides, that it is by no means certain that it has the foregoing simple configuration. Its reactions would be equally well indicated by the more complex

formula $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_5) \cdot \text{N}:\text{N} \\ \text{N}:\text{N} \cdot \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_5) \cdot \text{CH}_2 \end{array} \right\rangle \text{C}_6\text{H}_4$, in which the condensation is assumed to occur between two molecules of the diazonium base. The hydrogen of the acylamino-group, $\text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$, is certainly involved in the condensation, for when it is replaced by methyl, no diazo-anhydride is produced (compare p. 1166).

Benzenesulphonyl- ω -aminotoluene-3-azo- β -naphthol,

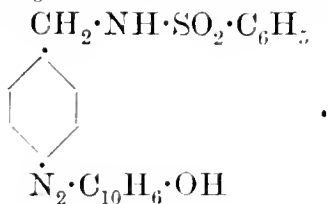


The filtrate from the preceding condensation product, when poured into alkaline β -naphthol containing a moderate excess of caustic alkali, immediately gave a scarlet precipitate of the azo-derivative, the amount of which showed that the greater portion of the diazonium chloride had not undergone condensation or any other radical change. The compound, when recrystallised from benzene, separated in small, red, flattened needles melting at 170—172°.

0.1130 gave 10.2 c.c. nitrogen at 17° and 764 mm. $\text{N} = 10.62$.

$\text{C}_{23}\text{H}_{19}\text{O}_3\text{N}_3\text{S}$ requires $\text{N} = 10.09$ per cent.

Benzenesulphonyl- ω -aminotoluene-4-azo- β -naphthol,



ω -Benzenesulphonyl-*p*-aminobenzylamine, when diazotised like its

isomerides, gave rise to a soluble diazonium chloride, the solution of which, when diluted and treated successively with sodium acetate and potassium hydrogen carbonate, yielded no insoluble condensation product and, on mixing with alkaline β -naphthol, furnished sufficient of the azo- β -naphthol derivative to show that the diazo-compound had not been affected by the acetate or bicarbonate. The azo-derivative was quite insoluble in water and crystallised from glacial acetic acid, benzene, or alcohol, separating from the last of these solvents in orange-red needles or prismatic crystals; its solutions in the other media deposited minute, felted needles.

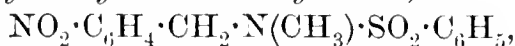
0.2034 gave 18.2 c.c. nitrogen at 19.5° and 765 mm. $N = 10.34$.

$C_{23}H_{19}O_3N_3S$ requires $N = 10.09$ per cent.

This compound, which melts at 188° , varies considerably in colour and crystalline form, sometimes separating from its solvents in dark red prisms. The three foregoing azo-derivatives all develop intense purple colorations with cold concentrated sulphuric acid; they dissolve in a moderate excess of caustic alkali to form sparingly soluble alkali salts which are precipitated by a large excess of the alkali. The ortho- and para-salts are readily hydrolysed by water, regenerating the free azo- β -naphthol; the meta-derivative is dissociated much less readily.

*Preparation of ω -Benzenesulphonyl- ω -methyl-*o*- and *m*-aminobenzylamines.*

*Benzenesulphonylmethyl-*o*-nitrobenzylamine,*



was prepared by heating together in alcoholic solution benzenesulphonyl-*o*-nitrobenzylamine (1 mol.), potassium hydroxide (1 mol.), and methyl iodide (1.5 mols.). During two and a half hours, no appreciable change occurred, but subsequently the contents of the flask became nearly solid. The alcohol was removed by evaporation, the solid product extracted with dilute aqueous caustic soda, and the residue, which consisted of almost colourless needles, crystallised with extreme readiness from either benzene or alcohol. The methylated nitro-compound was thus obtained in colourless, lustrous needles melting at $140-141^\circ$. The yield was practically quantitative.

0.2572 gave 20.6 c.c. nitrogen at 23° and 762 mm. $N = 9.06$.

$C_{14}H_{14}O_4N_2S$ requires $N = 9.15$ per cent.

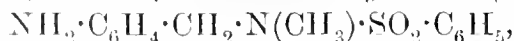
*Benzenesulphonylmethyl-*m*-nitrobenzylamine* was obtained in quantitative yield by heating benzenesulphonyl-*m*-nitrobenzylamine in alcoholic solution with the calculated amounts of caustic potash and methyl iodide.

After boiling the solution for six hours in a reflux apparatus, the liquid was cooled, when the whole became nearly solid owing to the separation of almost colourless needles of the methylated product; this compound when recrystallised from dilute alcohol separated in fern-like aggregates of colourless, transparent plates melting at 128° .

0.1959 gave 15.5 c.c. nitrogen at 22° and 769 mm. $N = 9.07$.

$C_{14}H_{14}O_4N_2S$ requires $N = 9.15$ per cent.

ω -Benzenesulphonyl- ω -methyl-o-aminobenzylamine (IX),



was prepared by reducing 2 grams of nitro-base with 4 grams of iron, 2 c.c. of glacial acetic acid, and 50 c.c. of hot water. After boiling for thirty-five minutes and neutralising with sodium carbonate, the reduction was quite complete, the insoluble residue on extraction with alcohol yielding an almost theoretical amount of the diamine. The base is very soluble in alcohol, although dissolving only sparingly in hot water; it crystallises best from dilute alcohol, separating from this solvent in colourless, nacreous leaflets or transparent plates melting at $108-110^{\circ}$.

0.2594 gave 23.0 c.c. nitrogen at 21° and 771 mm. $N = 10.24$.

0.2596 „ 0.2320 $BaSO_4$. $S = 12.27$.

$C_{14}H_{16}O_2N_2S$ requires $N = 10.14$; $S = 11.60$ per cent.

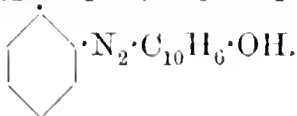
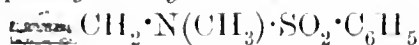
ω -Benzenesulphonyl- ω -methyl-m-aminobenzylamine (X), when obtained from the corresponding nitro-compound by the method described for its ortho-isomeride, crystallised from both aqueous and alcoholic extracts in colourless, glistening leaflets, the yield being practically quantitative. It is much less soluble in alcohol than the unmethylated base, and separates from this solvent in lustrous, lath-like crystals melting at $128-129^{\circ}$. This melting point is practically identical with that of the nitro compound, but a mixture of the two substances melts at 110° .

0.1413 gave 12.8 c.c. nitrogen at 22° and 769 mm. $N = 10.37$.

0.2342 „ 0.2114 $BaSO_4$. $S = 12.39$.

$C_{14}H_{16}O_2N_2S$ requires $N = 10.14$; $S = 11.60$ per cent.

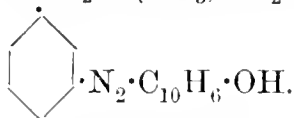
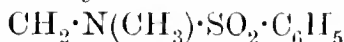
Diazotisation of the ω -Benzenesulphonyl- ω -methylaminobenzylamines.—The two foregoing ω -benzenesulphonyl- ω -methylaminobenzylamines behave similarly when treated with excess of cold concentrated hydrochloric acid and sodium nitrite, colourless solutions of soluble diazonium chlorides being obtained in both cases. These solutions are quite stable on dilution, and furnish no precipitate on successive treatment with sodium acetate and potassium hydrogen carbonate, but on pouring into alkaline β -naphthol solution the azo-derivatives are at once produced as orange-red precipitates.

Benzenesulphonylmethyl- ω -aminotoluene-2-azo- β -naphthol,

This azo-derivative crystallises well from benzene in scarlet lamellae melting at 188—189°.

0.2128 gave 18.7 c.c. nitrogen at 21° and 772 mm. $\text{N} = 10.11$.

$\text{C}_{24}\text{H}_{21}\text{O}_3\text{N}_3\text{S}$ requires $\text{N} = 9.74$ per cent.

Benzenesulphonylmethyl- ω -aminotoluene-3-azo- β -naphthol,

This substance, which separates from alkaline solutions as a somewhat viscid, orange-red precipitate, crystallises readily from benzene in transparent, brownish-red, massive plates containing benzene of crystallisation; the solvent is expelled at 100° and the residue melts very indefinitely at 150—160°.

0.6395 lost 0.0983 in the steam oven. $\text{C}_6\text{H}_6 = 15.37$.

0.3322 gave 23.7 c.c. nitrogen at 20° and 769 mm. $\text{N} = 8.26$.

$\text{C}_{24}\text{H}_{21}\text{O}_3\text{N}_3\text{S}, \text{C}_6\text{H}_6$ requires $\text{C}_6\text{H}_6 = 15.32$; $\text{N} = 8.25$ per cent.

The two foregoing azo-derivatives develop intense crimson colorations with cold concentrated sulphuric acid.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

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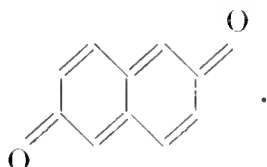
CXVI.—*The Mobility of Substituents in Derivatives of β -Naphthol.*

By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

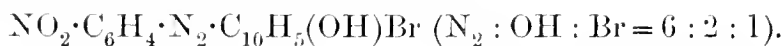
WHEN β -naphthol is subjected to the action of substituting agents, the hydrogen atom in position 1 is very readily replaced; the entrant group, if a halogen atom, is, however, also capable of easy displacement,

so that by dissolving a halogen-substituted β -naphthol in alkali and treating with the solution of a diazonium salt, halogen is eliminated and an azo-derivative of β -naphthol is precipitated. As will be seen in the sequel, this is apparently only a special case of mobility of α -substituents when introduced into the β -naphthol molecule.

A short explanation of the reasons which led to the trial of the reaction between substituted β -naphthols and diazonium salts is necessary. In cases where a phenol is converted into a hydroxyazo-compound, the entering azo-group occupies a position *ortho* or *para* to the hydroxyl of the phenol or naphthol employed. It occupies those positions, in fact, with respect to which a quinonoid structure is possible, or which would be occupied by nitro-groups if treatment with nitric acid had been resorted to. Thus, phenol and nitric acid give successively a mixture of *ortho*- and *para*-mono-nitro-derivatives and then 2:4-di-nitrophenol; whilst with a diazonium salt a mixture of *o*- and *p*-hydroxyazobenzenes (Bamberger, *Ber.*, 1900, **33**, 1950, 3188, 3192) and phenol-2:4-disazobenzene are successively obtained (Griess, *Ber.*, 1876, **9**, 628). When β -naphthol is nitrated, 1:6-dinitro-2-naphthol is always produced to a certain extent (Wichelhaus, *Ber.*, 1870, **3**, 846), and a quinonoid structure between the 2- and 6-positions is quite conceivable; in fact, it might perhaps be possible to oxidise 2:6-dihydroxynaphthalene to a new 2:6-naphthoquinone,



Bearing this in mind, we thought it worth while to act on an alkaline solution of a 1-substituted-2-naphthol with the solution of a diazonium salt, and chose 1-bromo-2-naphthol and diazotised *p*-nitro-aniline with which to carry out the experiment: the former on account of the ease with which it may be obtained, the latter on account of its stability and the well-defined physical properties which are usually associated with azo-derivatives obtained from it. We expected that coupling, if it occurred, would be slow, but that the resulting compound would possess the structure



To our surprise, coupling was very rapid; but the substance produced, when purified, was found to be free from halogen and to exhibit all the properties of *p*-nitrobenzeneazo- β -naphthol. During the progress of this investigation, a paper appeared describing the preparation and properties of 1-methyl-2-naphthol (*Ber.*, 1906, **39**, 435), it being demonstrated by K. Fries and E. Hübner that this substance will not

react with diazonium salts in alkaline solution. The alkyl group is evidently more firmly attached to the naphthalene nucleus than are halogen atoms, but that other groups besides halogens may be displaced from the α -position is rendered evident by the formation of 1:6-dinitro- β -naphthol when benzeneazo- β -naphthol is warmed with dilute nitric acid (Hewitt and Auld, *Trans.*, 1902, **81**, 1203), a similar result having been previously obtained by Zincke and Rathgen, who employed concentrated nitric acid (*Ber.*, 1886, **19**, 2484). It is therefore quite probable that the conversion of nitroso- β -naphthol into mono- and di-nitronaphthols by the action of nitric acid is to be regarded as a substitution of the nitroso- by the nitro-group rather than as a direct oxidation.

Amongst other replacements of α -substituents, the following cases may be mentioned: the conversion of benzeneazo- β -naphthyl-ethyl ether into the ethyl ether of 1:6-dinitro- β -naphthol (Meldola and Morgan, *Trans.*, 1889, **55**, 608), and the replacement of bromine by chlorine when *ana*-bromohydroxyquinolines are heated under pressure with hydrogen chloride (Howitz and Bärlocher, *Ber.*, 1905, **38**, 887, and Howitz and Witte, *ibid.*, 1260). The last result is of interest in that it shows that the mobility of the α -substituent seems to depend not so much on the character of the molecule chemically, but rather on its shape.

EXPERIMENTAL.

(1) *Preparation of p-Nitrobenzeneazo- β -naphthol from 1-Bromo-2-naphthol.*

Finely-powdered *p*-nitroaniline (13.8 grams) was stirred with 30 c.c. of fuming hydrochloric acid, cooled with ice, and diazotised by the gradual addition of 7.2 grams of sodium nitrite, dissolved in the minimal quantity of water. The resulting diazonium solution was decanted into an ice-cold solution of 1-bromo-2-naphthol (22.3 grams) in dilute caustic soda, containing excess of crystallised sodium acetate. Immediate coupling occurred, a brown product being precipitated. After filtration, the washed and dried azo-compound was crystallised first from glacial acetic acid and subsequently from toluene.

It then consisted of small, dark red crystals with a metallic-green reflex, obviously suggestive of ordinary *p*-nitrobenzeneazo- β -naphthol. It melted at 246° (uncorr.), a qualitative test for halogen gave a negative result, and the following numbers were obtained on analysis:

0.1467 gave 0.0507 H₂O and 0.3520 CO₂. C = 65.4; H = 3.8.

C₁₆H₁₁O₃N₃ requires C = 65.5; H = 3.8 per cent.

These results plainly indicated that the arylazo-group had displaced

the bromine atom, and the fact that this substance did not depress the melting point of a specimen of *p*-nitrobenzeneazo- β -naphthol, obtained from pure β -naphthol, establishes this quite conclusively.

In the experiment above described, *p*-nitroaniline had been chosen for diazotisation solely because a more convenient product was expected than would probably have been the case with aniline itself, the presence of a nitro-group in such compounds often materially enhancing their crystallising power.

Under the circumstances, however, we now felt compelled to establish the generality of this reaction by using

(a) Other diazotised amines.

(b) Other haloid naphthols.

The following experiments were therefore made :

(2) *Preparation of o-Nitrobenzeneazo- β -naphthol from 1-Bromo-2-naphthol.*

o-Nitroaniline was diazotised and added to an alkaline solution of 1-bromo-2-naphthol in a manner exactly analogous to that already described in the case of the *para*-isomeride.

Again coupling occurred immediately, just as if β -naphthol itself had been employed. The product, after two crystallisations from boiling glacial acetic acid, formed small, red needles and melted at 203° (uncorr.). This melting point agrees with that assigned by Meldola and Hughes (Trans., 1891, 59, 374) to *o*-nitrobenzeneazo- β -naphthol, and when mixed with a pure specimen of this compound, obtained from β -naphthol in the normal manner, no melting point depression was observed. The substance contained no halogen and gave the following results on analysis :

0.1199 gave 0.2863 CO₂ and 0.0439 H₂O. C = 65.1 ; H = 4.0.

C₁₆H₁₁O₃N₃ requires C = 65.5 ; H = 3.8 per cent.

(3) *Preparation of m-Nitrobenzeneazo- β -naphthol from 1-Bromo-2-naphthol.*

Diazotised *m*-nitroaniline instantly coupled with bromonaphthol in quite the same way, but in this case the purification of the product was a slightly more troublesome matter. However, after several recrystallisations from boiling glacial acetic acid, the substance was obtained as glistening, red crystals melting at 186° (uncorr.).

It contained no halogen, and gave the following figures on analysis :

0.1096 gave 0.2626 CO₂ and 0.0392 H₂O. C = 65.3 ; H = 3.9.

C₁₆H₁₁O₃N₃ requires C = 65.5 ; H = 3.8 per cent.

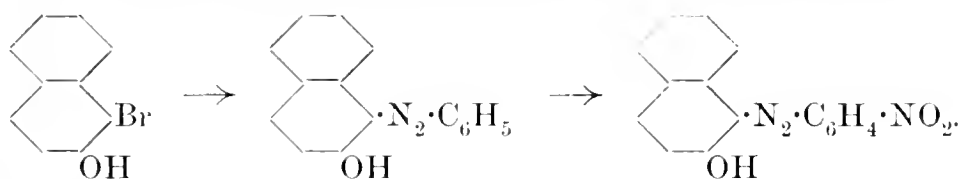
This compound, also, had been previously prepared by Meldola (Trans., 1884, **45**, 668), and from *m*-nitrophenyldiazonium chloride and β -naphthol we obtained a product melting at 192° (Meldola gives 194°). This specimen suffered no melting-point depression by admixture with the specimen obtained from the bromo- β -naphthol.

(4) *Attempted Preparation of Benzeneazo- β -naphthol from 1-Bromo-2-naphthol.*

Diazotised aniline was added to an alkaline solution of bromo-naphthol as usual. A brown product separated immediately, and was separated and dried. All attempts to obtain this substance in a crystalline condition were unsuccessful. At this we were not altogether surprised, benzeneazo- β -naphthol not possessing very strongly marked crystallising properties, even when in a fairly pure condition.

We therefore nitrated the crude product in strong sulphuric acid solution, one of the authors, in conjunction with S. J. M. Auld (Trans., 1902, **81**, 1202), having shown that the main product obtained by nitrating benzeneazo- β -naphthol under these conditions is the highly crystalline *p*-nitro-derivative.

The crude nitro-compound was dried and twice recrystallised from pyridine, the red, crystalline powder obtained in this way being washed with absolute alcohol, in which it was insoluble. Under the microscope it was seen closely to resemble *p*-nitrobenzeneazo- β -naphthol: it contained no halogen, and did not depress the melting point of a pure specimen of that substance. We therefore conclude that diazotised aniline reacted with bromonaphthol as in the other cases, the *p*-nitro-compound being isolated in accordance with the following scheme:



Several more experiments were made in a more qualitative manner, in order to demonstrate the perfectly general nature of the reaction; bromo- β -naphthol was found to react immediately with all the diazotised amines we employed, which included *o*-, *m*-, and *p*-toluidines, *p*-phenetidine, 2:4-dinitroaniline, β -naphthylamine, *o*- and *p*-amino-benzoic acids, β -naphthylamine-6- and -8-sulphonic acids.

(5) *Preparation of p-Nitrobenzeneazo- β -naphthol from 1-Iodo-2-naphthol.*

A pure specimen of 1-iodo-2-naphthol was prepared by Meldola's method (Trans., 1885, **47**, 525), the purity being controlled by a melting-point determination and by analysis.

On coupling this substance with diazotised *p*-nitroaniline and recrystallising the product from pyridine, red needles were obtained, melting at 247° (uncorr.). This specimen did not depress the melting point of pure *p*-nitrobenzeneazo- β -naphthol, contained no halógen, and gave the following analytical results :

0.1977 gave 0.4772 CO_2 and 0.0722 H_2O . $\text{C} = 65.8$; $\text{H} = 4.1$.

$\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3$ requires $\text{C} = 65.5$: $\text{H} = 3.8$ per cent.

(6) *Preparation of p-Nitrobenzeneazo- β -naphthol from 1-Chloro-2-naphthol.*

A pure specimen of 1-chloro-2-naphthol was obtained by chlorinating β -naphthol in chloroform solution and thrice recrystallising the product from light petroleum.

This was dissolved in alkali and treated with a *p*-nitrophenyldiazonium solution, just as in the other cases. Coupling occurred as in the previous experiments, the product after crystallisation from pyridine again proving to be the *p*-nitro-derivative of ordinary benzeneazo- β -naphthol.

As a final precaution, all four specimens of this substance, obtained respectively from (a) β -naphthol, (b) 1-chloro-2-naphthol, (c) 1-bromo-2-naphthol, (d) 1-iodo-2-naphthol, were ground to a paste with acetone, the acetone evaporated, and the melting point of the mixture taken. No depression was observed.

Action of Nitric Acid on Nitroso- β -naphthol.

1-Nitro-2-naphthol is obtained by the "oxidation" of nitroso- β -naphthol with nitric acid. We have tried the reaction between these substances under very varying conditions, and have noticed the production of dinitronaphthol in all cases when the temperature has been allowed to rise to about 40° or 50° . The yield was never satisfactory : in one case we obtained 2.3 grams of crude 1:6-dinitro- β -naphthol from 10 grams of the zinc salt of nitroso- β -naphthol and 40 c.c. of nitric acid of sp. gr. 1.5. This specimen, which had been isolated by the decomposition of its potassium salt with hydrochloric acid, melted at 174° ; after recrystallisation from ethyl acetate, the melting point rose to 190 (uncorr.) and the substance then gave the following results on analysis :

0.1118 gave 0.2119 CO_2 and 0.0291 H_2O . $\text{C} = 51.7$; $\text{H} = 2.9$.

$\text{C}_{10}\text{H}_6\text{O}_5\text{N}_2$ requires $\text{C} = 51.3$: $\text{H} = 2.6$ per cent.

The rate at which oxides of nitrogen are expelled from the reacting mass when nitroso- β -naphthol is added to concentrated nitric acid leads us to the belief that we have to deal here with the rapid dis-

placement of a nitroso-group by a nitro-group rather than with an oxidation, which from analogy might be expected to proceed more slowly.

Note.—During the course of this work we had occasion to prepare bromo- β -naphthyl acetate, a substance which has been described as a liquid by Canzoneri (*Gazzetta*, 1882, **12**, 431). We find that the substance, like the corresponding chloro- β -naphthyl acetate (Zincke and Kegel, *Ber.*, 1888, **21**, 3285), is a crystalline solid. Bromo-naphthol was warmed for a whole day on the water-bath with its own weight of acetic anhydride; the melt on pouring into water did not solidify for three weeks, when it set to a highly crystalline mass. On solution in alcohol and evaporation, no crystals were deposited for about a fortnight, when large prisms made their appearance. When one is in possession of some of the solid substance, no difficulty is experienced in recrystallising a new preparation, since its alcoholic solution may be sown with a fragment of the solid. The substance melts at 56° and is soluble in the usual organic solvents, including light petroleum.

0.1718 gave 0.3419 CO_2 and 0.0530 H_2O . $\text{C} = 54.3$; $\text{H} = 3.4$.

0.4589 „ 0.3249 AgBr . $\text{Br} = 30.1$.

$\text{C}_{12}\text{H}_9\text{O}_2\text{Br}$ requires $\text{C} = 54.3$; $\text{H} = 3.4$; $\text{Br} = 30.2$ per cent.

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CXVII.—*A Possible Source of Error in Stas' Nitrogen Ratios.*

By ROBERT WHYTLAW GRAY.

IN discussing the atomic weight of nitrogen, the International Committee on Atomic Weights in their Report for 1906 contrast the value obtained for this element by Rayleigh, Ledue, D. Berthelot, Guye, and myself with the value determined by Stas and other chemists. They state that there is much evidence in favour of both values, and they suggest that should Guye's conclusions respecting the atomic weight of silver prove correct, the new number for this element would bring the higher results for nitrogen in agreement with the lower.

It appears to the author of this paper, after a careful study of much experimental evidence, that this point is capable of an alternative explanation, and that the bulk of the data can be shown to support the

lower value for nitrogen without requiring the assumption of a lower value for silver. To set forth this view is the object of this communication.

To summarise the evidence for the lower constant for the element discussed, we have:

I Physical values:

	Ratios.	Atomic weight.
Rayleigh, Leduc, and D. Berthelot, $N_2 : O_2$		14·007
Recalculated in a different manner by Guye, $N_2 : O_2$ and $N_2 : CO$		14·009
Guye, $N_2O : CO_2$		14·007
R. W. Gray (including new unpublished $NO : O_2$ determinations)		14·009

II.* Chemical values:

	Ratios.	Atomic weight.
Guye	$N_2O : O$, $N_2 : O$, $N_2O : N$	14·010
R. W. Gray	$NO : O$, $N : O$, $NO : N$	14·010

The chemical values are supported by evidence from another source.

Marignac (*Œuvres complètes*, vol. I, p. 89).

	Atomic weight.
From the ratio $Ag : AgNO_3$, if $Ag = 107·93$	14·010

Scott (Trans., 1901, **79**, 147, and Proc., 1905, **21**, 309).

I. From the ratio $Ag : NH_4Cl$

II. „ „ „ $Ag : NH_4Br$

When $Ag = 107·93$; $Cl = 35·473$; $Br = 79·955$; $H = 1·0076$.

Richards and Archibald' (*Zeit. anorg. Chem.*, 1904, **34**, 353).

Taking $K = 39·122$, found by Archibald (*Trans. Roy. Soc. Canada*, 1904, sect. iii, 47), $Cl = 35·473$; $Ag = 107·93$.

	Atomic weight.
I. From the ratio $N_2O_5 : K_2O$	14·017
II. From a preliminary value determined from $Na_2CO_3 : 2NaNO_3$ (see <i>Proc. Am. Phil. Soc.</i> , 1904, 43 , 116)	14·02

Hence for a mean chemical value, we have:

Marignac	14·010
Scott	14·011
Richards	14·017
Guye	14·010
R. W. Gray	14·010

Mean 14·012

* For references, see paper already published (Trans., 1905, **87**, 1601).

and this number approximates closely to the mean result deduced from physical measurements, namely, 14.008.

From these two means, one deduces a final value

$$N = 14.010,$$

based on the data of no less than seven independent investigators.

Now if this value be accepted as correct, one is confronted with the difficulty of discovering the source of error in Stas' researches which led to an inaccurate result for this atomic weight.

According to Guye (*loc. cit.*), it is questionable whether the individual links in Stas' chain of ratios are known with sufficient exactness to estimate correctly the second place of decimals in the atomic weight of nitrogen. On the other hand, Stas' different values for this constant show a remarkable concordance.

Admitting that the ratios have been measured with the requisite degree of accuracy, there are three ways in which this error may have originated.

(a) Stas' atomic weight of silver may be incorrect. That is to say, the ratio Ag:O, depending solely on the analysis of a few oxyhalogen salts, may be at fault. An error in this link of the chain would mean that Stas' nitrogen values referred through silver to oxygen are expressed in terms of a different standard to those of Guye, which are referred directly to oxygen.

(b) It is possible that the standards are exactly commensurable, but the error lies in one or more of the chemical ratios which connect silver with nitrogen.

(c) The total error may be due to an error in the atomic weight of silver combined with one or more errors in the other ratios.

From the point of view of (a), a discussion of the atomic weight of silver by Guye in the paper already quoted is of great interest. This constant was recalculated from a number of ratios involving nitrogen taken from the experiments of Penny, Marignac, Stas, and others. The value for nitrogen was taken to be 14.009. Further calculations were made of the atomic weight of silver from analyses of its organic salts, using the determinations of Liebig and Redtenbacher and other workers. The two sets of numbers deduced agreed with each other, and the mean atomic weight of silver was found to be 107.885. From this result, Guye concluded that Stas' Ag:O ratio is erroneous. This conclusion, however, accounts only imperfectly for Stas' nitrogen values.

Consider the following ratios taken from the latest determinations of Stas.

		Ag=107.93.	Ag=107.885.
(1)	Ag : AgCl = 100 : 132.850.....	Cl = 35.455	35.440
(2)	Ag : NaCl = 100 : 54.205.....	Na = 23.048	23.039
(3)	Ag : KCl = 100 : 69.119.....	K = 39.145	39.129
(4)	Ag : NaBr = 100 : 95.438	Br = 79.958	79.924

If these atomic weights reduced to the standard Ag=107.885 (last column) are used to calculate the atomic weight of nitrogen in the other Stas determinations, we obtain :

		Ag=107.93.	Ag=107.885.
(5)	Ag : AgNO ₃ = 100 : 157.495	N = 14.054	14.039
(6)	NaCl : NaNO ₃ = 100 : 145.468	N = 14.055	14.029
(7)	KCl : KNO ₃ = 100 : 135.642	N = 14.044	14.018
* (8)	Ag : NH ₄ Cl = 100 : 49.599	N = 14.047	14.041
(9)	Ag : NH ₄ Br = 100 : 90.830	N = 14.045	14.029
	Mean	14.049	14.031

* H=1.0076.

It is hence apparent that the assumption of a lower atomic value for silver does not entirely explain the discrepancy.

Possibility (b) must therefore be considered.

Recent researches have shown that Stas' results for chlorine and sodium are probably slightly incorrect, and the question arises : can the high atomic weight of nitrogen be due to this cause ?

The revised atomic weights of sodium and chlorine and the resulting value for potassium can be deduced from the following ratios :

		Ag=107.93.
(10)	Richards and Wells (<i>loc. cit.</i>).....	Ag : AgCl = 100 : 132.867 Cl = 35.473
(11)	{ Ag : NaCl = 100 : 54.185 } { AgCl : NaCl = 100 : 40.780 }	Na = 23.008
(12)	Archibald (<i>loc. cit.</i>) { Ag : KCl = 100 : 69.114 } { AgCl : KCl = 100 : 52.025 }	K = 39.122

If one assumes the correctness of Stas' value for bromine expressed in the same standard, namely, 79.955, a number confirmed recently by G. P. Baxter (*J. Amer. Chem. Soc.*, 1905, 28, No. 7), the following numbers result when the revised values for Cl, K, and Na are used to calculate Stas' nitrogen.

(6)	NaCl : NaNO ₃	N = 14.041
(7)	KCl : KNO ₃	N = 14.060
(8)	Ag : NH ₄ Cl.....	N = 14.029
(9)	Ag : NH ₄ Br.....	N = 14.047
	Mean	14.044

It is hence manifest that errors in the ratios $\text{Ag} : \text{AgCl}$ and $\text{Ag} : \text{NaCl}$ also fail to explain the results for nitrogen.

There still remains possibility (c), namely, that the new atomic weight for chlorine, sodium, and potassium, when reduced to the standard $\text{Ag} = 107.885$ and applied to the foregoing ratios (6), (7), (8), and (9), may yield a solution of the problem.

The new atomic weights reduced to $\text{Ag} = 107.885$ are :

$$\text{Cl} = 35.459, \text{Na} = 22.996, \text{K} = 39.110, \text{Br} = 79.921,$$

and hence the results :

(6) $\text{NaCl} : \text{NaNO}_3$	$\text{N} = 14.037$
(7) $\text{KCl} : \text{KNO}_3$	$\text{N} = 14.037$
(8) $\text{Ag} : \text{NH}_4\text{Cl}$	$\text{N} = 14.021$
(9) $\text{Ag} : \text{NH}_4\text{Br}$	$\text{N} = 14.041$
Mean	<hr/> 14.034

Hence the difficulty is explained by none of these three possibilities, (a), (b), or (c).

Is it likely, then, that the atomic weight of silver can lie below 107.885? From Guye's calculations, this does not seem probable. An examination of the question in the light of the latest measurements tends rather to a higher value for this constant.

Consider the ratio of Stas' $\text{Ag} : \text{AgNO}_3 = 100 : 157.495$. In order to find $\text{N} = 14.009$, one must postulate $\text{Ag} = 107.85$.

On this assumption, the atomic weight of chlorine would become :

	Atomic weight.
From the ratios of Stas	35.429
„ „ „ „ Richards and Wells	35.447

Now even the higher of these two values is in all probability distinctly too low, for Dixon and Edgar (*Phil. Trans.*, 1905, *A*, 205, 169) have measured directly the ratio $\text{H} : \text{Cl}$, and by combining this result with the ratio $\text{O} : \text{H}$, fixed with great exactness by many researches, they have obtained

$$\text{O} : \text{Cl} = 16 : 35.463.$$

This value is confirmed by Scott's $\text{Ag} : \text{NH}_4\text{Cl}$ ratio (*loc. cit.*), for if one assumes $\text{N} = 14.009$, one obtains, when $\text{Ag} = 107.93$,

$$\text{Cl} = 35.467.$$

The experiments of Leduc on the physical constants of hydrochloric acid gas (*Ann. Chim. Phys.*, 1898, [vii], 15, 1) also confirm this value. He found

$$\text{Cl} = 35.470,$$

and a recalculation of his data by Guye gave (*Bull. Soc. chim.*, 1905, [iii], 33, 44)

$$\text{Cl} = 35.475.$$

It has hence been shown that the lowest possible value for the atomic weight of silver does not bring the results of Stas and Guye for nitrogen in accordance. Neither is the difficulty explained by the errors discovered by Richards and Wells in Stas' atomic weights of sodium, chlorine, and potassium, whilst a combination of the suggested silver standard with the new values for these three elements yields no better solution of the problem.

The error then must lie in the Stas ratios linking nitrogen with other elements. They are:



Of these equivalent numbers, the two first are probably erroneous when considered in the light of the same ratios remeasured by Scott (*loc. cit.*).

This investigator found $\text{Ag} : \text{NH}_4\text{Cl} = 100 : 49.584$, $\text{Ag} : \text{NH}_4\text{Br} = 100 : 90.795$; whilst Stas obtained $100 : 49.599$, $100 : 90.830$.

What, then, is the explanation of the larger amounts of ammonium chloride and ammonium bromide found by Stas to unite with 100 parts of silver?

A clue to the solution of this problem can be found in the work of Richards and Wells (*loc. cit.*).

Comparing the ratios

Richards and Wells.	Stas.
$\text{Ag} : \text{NaCl} = 100 : 54.185$	$100 : 54.205$

one notices that the difference in the numbers for sodium chloride is of the same order as the difference between Scott and Stas' numbers for the foregoing ratios.

A minute investigation of this difference convinced Richards and Wells that the error in Stas' work was due:

(1) To the occlusion of some sodium chloride by the precipitated silver chloride.

(2) To a too early reading of the opalescence in the last stages of a titration which led to an erroneous end-point.

(3) To the presence of traces of platinum in the sodium chloride.

It was found experimentally that the quantity of sodium chloride occluded or absorbed by the silver chloride in an experiment carried out in the same manner precisely as Stas used in his later determinations was 0.015 per cent. of the weight of sodium chloride taken. The opalescence error was estimated for sodium chloride to be about five-sevenths of this, namely, 0.011 per cent., and the error due to platinum

of about the same magnitude, namely, 0·015 per cent. Bearing in mind that Stas determined several of his other ratios in precisely the same way as the Ag : NaCl ratio, namely, Ag : NH₄Cl, Ag : NH₄Br, Ag : NaBr, Ag : KBr, and Ag : KCl, it is possible to calculate an approximate correction and apply it to these numbers. This correction can only be regarded as a rough approximation, for experiments may show that the occlusion and opalescence errors are by no means of the same order of magnitude for other reactions as for that between silver nitrate and sodium chloride. The presence of platinum in the other salts is even less certain.

It must be remembered, however, that a large error in the correction only slightly affects the resulting atomic weight.

Bearing these reservations in mind, we have :

For Stas' ratio Ag : NH₄Cl = 100 : 49·599.

Occlusion error	$\frac{0\cdot015 \times 49\cdot6}{100}$	0·0074
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Platinum error	0·0074
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Opalescence error	$1\cdot0074 \times \frac{5}{7}$	0·0053
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A. Total error.....	0·0201
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B. Or total error omitting platinum correction ...	0·0127
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Hence Stas' ratio becomes :

$$\text{Ag} = 107\cdot93, \quad \text{Cl} = 35\cdot473.$$

A. Ag : NH₄Cl = 100 : 49·579. N = 14·007.

B. „ „ = 100 : 49·586. N = 14·015.

The mean of these values is very near Scott's ratio already quoted.

For Stas' ratio Ag : NH₄Br = 100 : 90·830, the errors are :

Occlusion error	$\frac{0\cdot015 \times 90\cdot8}{100}$	0·014
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Opalescence error	$0\cdot014 \times \frac{5}{7}$	0·010
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Platinum	0·011
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and the ratio becomes

$$\text{Ag} = 107\cdot93; \quad \text{Br} = 79\cdot955.$$

Corrected A. Ag : NH₄Br = 100 : 90·792. N = 14·006.

„ B. „ „ = 100 : 90·802. N = 14·017.

Hence mean corrected atomic weight of nitrogen deduced from Stas' measurements	} becomes 14·011.

From the other ratios one obtains, by correcting in the same manner :

A. Ag : NaBr.	Na = 23·009	} Mean 23·016.
B. „ „	Na = 23·024	
A. Ag : KCl.	K = 39·097	} Mean 39·103.
B. „ „	K = 39·114	
A. Ag : KBr.	K = 39·092	
B. „ „	K = 39·110	

It is hence apparent that the number for sodium approximates closely to Richards and Wells' value, namely, $\text{Na} = 23\cdot008$. The value for potassium agrees well with that deduced from Stas' ratio, $\text{KClO}_3 : \text{KCl} = 100 : 60\cdot843$ when $\text{Cl} = 35\cdot473$, namely, $\text{K} = 39\cdot110$. On the other hand, this atomic weight is distinctly lower than the value recently found by Archibald (*loc. cit.*), namely: $\text{K} = 39\cdot122$ when $\text{Cl} = 35\cdot473$. The latter number for potassium agrees with the mean value resulting from the above tabulated equivalents of Stas when uncorrected if the same number for chlorine be used. Hence the question may be asked: are the errors then discovered by Richards and Wells for the $\text{Ag} : \text{NaCl}$ ratio non-existent in the ratio $\text{Ag} : \text{KCl}$? It is also noteworthy that Penny's researches led to an atomic weight for potassium lying below $39\cdot10$.

If the foregoing deductions really explain Stas' error in the atomic weight of nitrogen for the equivalent numbers considered, and from the measurements of Scott it seems probable that they do, there remain only three more ratios to be considered, namely:



For the first of the three Stas found:

		$\text{Ag} = 107\cdot93$	
Earlier results (salt fused)	$\text{Ag} : \text{AgNO}_3 = 100 : 157\cdot472.$	$\text{N} = 14\cdot029$	
Later „ (salt dried)	„ „ „ $= 100 : 157\cdot495.$	$\text{N} = 14\cdot054$	
But Marignac found	„ „ „ $= 100 : 157\cdot455.$	$\text{N} = 14\cdot011$	
And Penny *	„ „ „ $= 100 : 157\cdot441.$	$\text{N} = 14\cdot000$	

Hence it may be questioned whether Stas' numbers are as exact as he claimed.

Putting this ratio aside as not above suspicion, the two remaining series of determinations must be considered.

	$\text{Na} = 23\cdot008.$	$\text{Cl} = 35\cdot473.$	$\text{K} = 39\cdot122.$
Stas found	$\text{KCl} : \text{KNO}_3 = 100 : 135\cdot642.$	$\text{N} = 14\cdot060$	
Penny „	„ „ „ $= 100 : 135\cdot636.$	$\text{N} = 14\cdot056$	
Stas „	$\text{NaCl} : \text{NaNO}_3 = 100 : 145\cdot468.$	$\text{N} = 14\cdot041$	
Penny „	„ „ „ $= 100 : 145\cdot410.$	$\text{N} = 14\cdot029$	

* *Phil. Trans.*, 1839, **129**, i, 32.

Although the potassium equivalents of Stas and Penny agree perfectly, the sodium ratios exhibit a marked divergence. Still the resulting values for nitrogen approximate to the higher number. For these results no explanation can be offered. No likely variation of the atomic weights involved can account for the discrepancy.

Did the halide salts contain an impurity which was converted into a higher state of oxidation on treatment with nitric acid? Did the nitrates weighed contain traces of occluded water? Many possibilities of this kind suggest themselves. As is well known, Stas consistently obtained lower results for his nitrate ratios when the nitrate was fused before weighing. It seems probable that future measurements will reveal an error of this nature in these equivalent numbers, but in the absence of more data it is unwise to speculate.

To sum up: there is much evidence to show that the results of Stas for the atomic weight of nitrogen are erroneous.

His different ratios interpreted in the light of modern researches do not yield consistent values for this element.

An examination of his experiments leads to the conclusion that the source of error lies in the equivalent numbers connecting nitrogen with other elements.

Of the ratios considered, $\text{Ag} : \text{NH}_4\text{Cl}$ and $\text{Ag} : \text{NH}_4\text{Br}$ admit of an approximate correction, and the validity of this correction is confirmed by the close agreement of the results with those of Scott for the same ratios.

The correctness of Stas' $\text{Ag} : \text{AgNO}_3$ numbers is questioned, for it is not in accordance with the results of Marignac and of Penny.

The values obtained for $\text{NaCl} : \text{NaNO}_3$ and for $\text{KCl} : \text{KNO}_3$ are concluded to be infected with an error of which account cannot be taken.

The only confirmations of the higher value for nitrogen found by Stas are :

- (1) The experiments of Penny already quoted.
- (2) The value obtained by Richards and Archibald for the ratio,

$$\text{N}_2\text{O}_5 : \text{Cs}_2\text{O} = 100 : 260.693.$$

If $\text{Cs} = 132.879$; $\text{N} = 14.037$.

And this is not in agreement with their result deduced from $\text{N}_2\text{O}_5 : \text{K}_2\text{O}$ by the same method, namely, $\text{N} = 14.017$ if $\text{K} = 39.122$.

(3) The number obtained by Dean (Trans., 1900, 77, 117) from the ratio $\text{AgCN} : \text{Ag}$, $\text{N} = 14.031$.

It is therefore concluded that the higher value for this constant is supported by very little evidence. The correctness of the lower value is rendered highly probable, not only by the agreement obtained between

the results of physical measurement and direct chemical analysis, but also by the results yielded by several indirect comparisons of the atomic weights of nitrogen and silver.

CXVIII.—*The Decomposition of Nitrocellulose.*

By OSWALD SILBERRAD, Ph.D., and ROBERT CROSBIE FARMER,
Ph.D., D.Sc.

THE products resulting from the gradual deterioration of nitrocellulose on storage have for many years formed the subject of investigation by different workers. Nitrous and nitric acids are at once recognised, but as to the nature of the organic compounds formed, very little is known with certainty, the reactions being complicated and the substances difficult to separate.

The principal investigations on this subject are those of Kerckhoff (*J. pr. Chem.*, 1847, **40**, 284), Maurey (*Compt. rend.*, 1849, **28**, 343), Vohl (*Dingl. polyt. Journ.*, 1849, **112**, 236), Hadow (*Trans.*, 1854, **7**, 201), Béchamp (*Compt. rend.*, 1855, **41**, 817; *Ann. Chim. Phys.*, 1856, **46**, 338; *Bull. Soc. chim.*, 1863, **5**, 289), Hofmann (*Annalen*, 1860, **115**, 283), De Luca (*Compt. rend.*, 1861, **53**, 298; 1864, **59**, 487), Bonet (*Compt. rend.*, 1861, **53**, 405), Divers (*Trans.*, 1863, **16**, 91), Pelouze and Maurey (*Compt. rend.*, 1864, **59**, 363), Blondeau (*Compt. rend.*, 1864, **59**, 963; 1865, **60**, 128), Abel (*Phil. Trans.*, 1867, 182), Will (*Ber.*, 1891, **24**, 400, 3831), and Häussermann (*Ber.*, 1903, **36**, 3956; 1904, **37**, 1624). In all of these investigations the amount of nitrocellulose taken was relatively small, and it was considered advisable in the present work to employ a much larger quantity in order to render possible the isolation of products which occur only to a small extent.

The compounds identified were as follows: ethyl nitrate, ethyl nitrite, ethyl alcohol, nitric and nitrous acids, ammonia, formic, acetic, butyric, dihydroxybutyric, oxalic, tartaric, isosaccharinic, and hydroxypyruvic acids. Carbohydrates were found to be present by the fermentation test, and certain other compounds were obtained, but could not be identified by reason of the complexity of the mixture and their minute quantity.

EXPERIMENTAL.

A quantity of 800 kilograms of a gelatinised nitrocellulose was stored in a magazine which was maintained at 54.4° (130° F.) by means of steam pipes, the flow of steam being regulated electrically,

so that the temperature did not deviate more than 1° from the mean. Part of the steam was blown directly into the chamber containing the powder in order to supply enough moisture to facilitate a hydrolysis of the nitric ester. After twenty-three weeks, a strongly marked deterioration had set in. In many instances, the tubular propellant was filled with a crystalline deposit which was found to consist of almost pure oxalic acid.

One hundred kilograms of the nitrocellulose were taken for the chemical investigation. Previous analyses had shown that the deterioration of nitrocellulose is accompanied by an increase in the amount of water-soluble matter, and thus it appeared that the best method of extracting the decomposition products would be to treat the powder with water. It was accordingly heated to 80° with an equal weight of water, and the aqueous solution filtered. The decomposition products were, for the most part, extracted by the water, and the residue apparently consisted of almost unaltered nitrocellulose, as is shown by the following analysis:

Analysis of Residue after Extraction with Water.

	Unheated sample dried at 80° . Per cent.	Insoluble residue after extraction with water dried at 80° . Per cent.
Insoluble in ether-alcohol	8.05	8.35
Soluble in ether-alcohol.....	91.58	90.35
Insoluble in acetone	0.27	1.30
Nitrogen.....	12.34	12.02
Ignition point	200°	200°

For the separation of the decomposition products, the aqueous extract was first distilled to a quarter of its bulk. A portion of the distillate was tested for nitrous and nitric acids by the well-known reactions; both of these were found to be present in large quantity. The remainder of the distillate was redistilled with a fractionating column, and ethyl nitrate was ultimately isolated in a state of purity. Its identity was established by its properties and saponification products, as also by analysis:

Found, N = 15.66. $C_2H_5O_2N$ requires 15.41 per cent.

The presence of alcohol in excess of the nitric ester was proved by the iodoform reaction, and ethyl nitrite was detected by its characteristic odour. The presence of these products is due to the ether-alcohol used as gelatinising solvent in the manufacture of the powder.

The residue from the above distillation was saturated with calcium carbonate, concentrated, allowed to cool, and filtered. The semi-crys-

talline residue was dissolved in water, freed from calcium by precipitation with oxalic acid, filtered, and the filtrate saturated with barium carbonate. The excess was separated, the filtrate evaporated to dryness, and the ground residue extracted with alcohol. The insoluble part was dissolved in water, the barium precipitated as sulphate, and the filtrate saturated with calcium carbonate, again filtered, and evaporated to crystallisation. The salt was further purified by recrystallisation and consisted of calcium formate.

Found, $\text{Ca} = 30.68$. $\text{C}_2\text{H}_2\text{O}_4\text{Ca}$ requires $\text{Ca} = 30.82$ per cent.

The filtrate from the calcium formate was further concentrated and fractionally precipitated with alcohol. The least soluble fraction was dissolved in water and warmed with mercuric chloride. The mercurous chloride produced by the formic acid present was separated and the solution treated with oxalic acid to precipitate the calcium. The filtrate was saturated with barium carbonate, filtered, evaporated to dryness, and the dry powder extracted with alcohol. The residue was dissolved in water and the concentrated solution treated with silver nitrate; the precipitate thus obtained was thrown into boiling water to saturation, filtered rapidly, and allowed to cool, when long, needle-shaped crystals of silver acetate separated.

Found, $\text{Ag} = 64.82$. $\text{C}_2\text{H}_3\text{O}_2\text{Ag}$ requires $\text{Ag} = 64.57$ per cent.

The most soluble of the fractions obtained on precipitating with alcohol was dried and subjected to prolonged shaking with ice-cold water. The solution was filtered and heated to boiling, when a copious precipitate separated. This was removed from the hot solution; the filtrate was allowed to cool and again saturated with the crude fraction at 0° , filtered, and heated as before. The combined precipitates were dissolved in water and treated with silver nitrate. The precipitated salt agreed in its composition and properties with silver butyrate.

Found, $\text{Ag} = 55.82$. $\text{C}_4\text{H}_7\text{O}_2\text{Ag}$ requires $\text{Ag} = 55.35$ per cent.

The residual liquid from the original distillation was saturated with calcium carbonate, heated to boiling, and filtered. A distinct odour of ammonia was observed, and its presence was further confirmed by the Nessler test. The insoluble residue consisted of calcium oxalate and tartrate, which were separated in the usual manner.

Calcium oxalate dried at 210° .

Found, $\text{Ca} = 31.22$. $\text{C}_2\text{O}_4\text{Ca}$ requires $\text{Ca} = 31.30$ per cent.

Calcium tartrate.

Found, $\text{Ca} = 21.20$. $\text{C}_4\text{H}_4\text{O}_6\text{Ca}$ requires $\text{Ca} = 21.31$ per cent.

The filtrate from the calcium oxalate and tartrate was allowed to stand

for twelve hours at 0° , when a sparingly soluble mass separated out. This was dissolved in twenty-five times its weight of water, and the calcium precipitated by the addition of oxalic acid. The calcium oxalate was separated and the filtrate evaporated until only a gummy mass remained behind. This was dissolved in dilute alcohol. The alcohol was then very slowly concentrated by removing the water over quicklime in a vacuum. After some time, a semi-crystalline mass was obtained, and this, after further purification, melted at 92° . It agreed in all its properties with the lactone of isosaccharinic acid (m. p. 95).

Found, C = 44.12; H = 6.32.

$C_6H_{10}O_5$ requires C = 44.42; H = 6.22 per cent.

The filtrate from the calcium isosaccharinate was concentrated and allowed to stand, but no crystals were obtained. The solution was diluted with half its volume of alcohol, whereupon an amorphous, brown powder separated out. The filtrate yielded on treatment with lead acetate a mixture of insoluble salts which could not be further separated owing to its complexity. The residue from the alcoholic solution was washed with water and proved to be the salt of a complex acid whose properties did not agree with those of any known acid. It gave on analysis Ca = 12.48 per cent.

On treating the aqueous solution with phenylhydrazine in acetic acid solution, an insoluble compound was obtained. This was dissolved in caustic soda, filtered, reprecipitated with hydrochloric acid, and recrystallised from alcohol. It melted at 205° and proved to consist of the osazone of hydroxypyruvic acid.

Found, N = 19.67. $C_{15}H_{14}O_2N_4$ requires N = 19.89 per cent.

The filtrate from the osazone was rendered slightly alkaline with lime-water and shaken with ether to remove the excess of phenylhydrazine and various dark-coloured products. The aqueous solution was concentrated and precipitated by the addition of alcohol. The precipitate was redissolved in water and fractionally precipitated with alcohol, the middle fractions being retained throughout. In this way a pure salt was ultimately obtained whose properties agreed with those of calcium $\beta\gamma$ -dihydroxybutyrate.

The salt, after being dried at 110° , gave Ca = 14.06.

$C_8H_{14}O_5Ca$ requires 14.41 per cent.

In order to ascertain whether fermentable carbohydrates were present, a fresh portion of the nitrocellulose deteriorated by long storage was extracted with water. The aqueous extract was neutralised and distilled until all traces of alcohol were completely removed. Yeast was then added to the residual liquor and the mixture maintained

at about 25° and allowed to ferment. A considerable disengagement of carbon dioxide occurred. The residual liquid was distilled and the distillate treated with iodine and alkali. Iodoform was at once precipitated, showing that a fermentation had taken place.

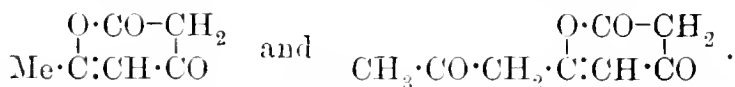
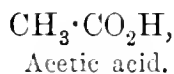
Our thanks are due to the Director of Artillery and to the Explosives Committee for permission to publish these results.

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CXIX.—*The Esters of Triacetic Lactone and Triacetic Acid.*

By FOSTER SPROXTON, B.Sc.

MUCH of the synthetic organic chemistry of recent years has centred round the compounds containing the group $-\text{CO}\cdot\text{CH}_2-$, and of these probably the most important is ethyl acetoacetate. This substance is the ethyl ester of the second member of what may be termed the polyacetic series, four members of which are known, namely,



δ -Lactone of triacetic acid. δ -Lactone of tetracetic acid (dehydracetic acid).

The esters of the first two compounds are, of course, well known, whilst methyl dehydracetate and ethyl dehydracetate were prepared by Perkin (*Trans.*, 1887, 51, 484) and Collie and Le Sueur (*Trans.*, 1894, 65, 254) respectively. The latter compounds possess properties not usually associated with esters. They dissolve in water, yielding solutions which give an acid reaction, and Perkin found (*loc. cit.*) that if solutions of methyl dehydracetate and sodium ethoxide in dry ether were mixed, a pink compound was precipitated. This he regarded as the sodium salt of the ester.

Apart, therefore, from the intrinsic interest of the esters of triacetic lactone and triacetic acid as members of an important series of organic compounds, it seemed possible that a study of their reactions might throw some light on the unusual properties of the analogous methyl and ethyl dehydracetates.

It has not, however, been found possible to prepare the ethyl salt of triacetic lactone in a pure condition, but the methyl ester of the lactone and the ethyl ester of triacetic acid have been prepared and their properties examined. It has been found that the esters of triacetic lactone, like those of dehydracetic acid, possess an acid reaction in aqueous solution. This property, however, in the case of both the tetracetic and triacetic lactone derivatives, has been shown to be due not to any acidity of the esters themselves, but to hydrolysis of these compounds by water. Perkin (*loc. cit.*) noticed that methyl dehydracetate was instantaneously saponified by cold potash, but that it should be hydrolysed by water alone is still more remarkable. There is, therefore, no need to assume that the pink compound which Perkin obtained by the action of sodium ethoxide on methyl dehydracetate is the sodium salt of the ester. Possibly it is a complicated dehydration product similar to those strongly coloured compounds known to be obtained by the action of solid sodium hydroxide and other compounds on dimethylpyrone (Collie, *Trans.*, 1904, 85, 974). The esters of triacetic lactone do not give similar coloured compounds with sodium ethoxide.

EXPERIMENTAL.

Ethyl Triacetate, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et}$.

Three methods were tried for the preparation of this compound, none of them being entirely satisfactory, as only small yields were obtained. The first consisted in passing dry hydrogen chloride through a warm alcoholic solution of triacetic lactone until a small portion of the solution left no crystalline residue on evaporation. The whole of the solution was then diluted with water and extracted with ether. After being dried over calcium chloride, the ether was evaporated on the water-bath and the residue distilled under diminished pressure. A small quantity of a yellow oil passed over between 130° and 140° at 20 mm. pressure. A solution of the oil in alcohol gave a deep red coloration with ferric chloride, and a sparingly soluble copper salt with cupric acetate and a little ammonia.

As the product obtained by this method was impure and the yield small, an attempt was made to prepare the compound by heating triacetic lactone with alcohol in a sealed tube. The tube was kept at 100 — 110° until triacetic lactone no longer crystallised out on cooling. With ordinary absolute alcohol, considerable decomposition took place, but when perfectly pure dry alcohol was employed, the tube opened without pressure. The alcoholic solution was then fractionated as before, but the yield was still small and impure.

It was finally found best to prepare the ester by decomposing its

copper salt by means of sulphuretted hydrogen. The copper salt (to be described afterwards) was suspended in water, and sulphuretted hydrogen passed through until all the copper had been converted into sulphide. This was separated and the ethyl triacetate extracted with ether. After drying the extract and evaporating the ether, first on the water-bath and finally in a vacuum, ethyl triacetate was left as a slightly yellow oil which could not be crystallised. Analysis gave: $C = 55.7$, $H = 7.08$; $C_8H_{12}O_4$ requires $C = 55.8$, $H = 6.98$ per cent.

The ester has an odour somewhat resembling that of ethyl acetate and is soluble in water, yielding a solution possessing a neutral reaction. An alcoholic solution develops a deep red coloration with ferric chloride. When heated alone, the compound decomposes, evolving carbon dioxide and alcohol, whilst a yellow, uncrystallisable oil remains which is soluble in caustic alkalis.

The absorption spectrum of ethyl triacetate was taken, and found to possess a strongly characterised enol-keto-band similar to that given by acetylacetone.

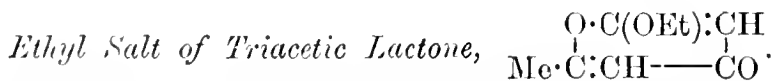
Copper Salt of Ethyl Triacetate.

Dry ethyl alcohol and triacetic lactone, when heated together under pressure, yield, as stated above, an alcoholic solution of ethyl triacetate. When cupric acetate, dissolved in alcohol with the addition of a little ammonia, is added to this solution, a copper salt slowly separates as a flocculent, blue precipitate consisting of fine, needle-shaped crystals. After filtering and washing once or twice with alcohol, the compound is obtained in the pure state. It dries to a light blue powder, melting and decomposing at $183-184^\circ$. A combustion and an estimation of the copper as cuprous sulphide gave the following result:

$C = 47.1$, $H = 5.47$, $Cu = 15.77$.

$C_{16}H_{22}O_8Cu$ requires $C = 47.4$, $H = 5.40$, $Cu = 15.70$ per cent.

Several attempts were made to prepare ethyl tetracetate by heating dehydracetic acid and alcohol in a sealed tube. It was found that a small quantity of some intensely yellow compound was found, but not sufficient was obtained to determine its properties.



To obtain this compound, the silver salt of triacetic lactone was suspended in alcohol and excess of dry ethyl iodide added. Care was taken to keep all the materials thoroughly dry, as in one or two early experiments only triacetic lactone was obtained from the reaction

mixture. The reaction was complete after heating under a reflux condenser for an hour. The silver iodide was removed by filtration and most of the alcohol and ethyl iodide distilled off. The residue was placed in a vacuum desiccator over sulphuric acid. A yellow oil with a characteristic odour remained, and after standing for a few days a solid substance began to separate. The mean of four closely-agreeing analyses of the product is given below :

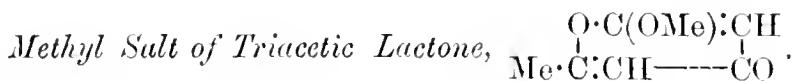
$$C = 60.9, H = 6.5.$$

$$C_6H_6O_3 \text{ requires } C = 57.1, H = 4.8.$$

$$C_8H_{10}O_3 \text{ requires } C = 62.3, H = 6.5 \text{ per cent.}$$

The product of the reaction was therefore a mixture of triacetic lactone and its ethyl ester, and it was not found possible to prepare a pure specimen of the latter. It is possible that even the slight acidity of ethyl iodide due to decomposition may be sufficient to decompose a considerable quantity of the ester.

The impure product gave no coloration with ferric chloride and yielded no copper salt. Since it contained triacetic lactone, its aqueous solution had of course an acid reaction. When boiled with a small amount of water and quickly cooled, pure triacetic lactone (m. p. 188°) crystallised out, showing that the ethyl salt is completely hydrolysed under these conditions.



It was found that this compound could be easily prepared in the pure state by the action of methyl iodide on the silver salt of the lactone suspended in dry methyl alcohol. Here also great care must be taken to keep the materials quite dry. Exactly the same method of procedure was adopted as in the last case, and on evaporating the alcohol in a vacuum over sulphuric acid a crystalline substance remained. This was recrystallised from dry ether and melted sharply at 81° . The crystals consist of tufts of colourless needles closely resembling triacetic lactone.

$$C = 60.0, H = 5.76.$$

$$C_7H_8O_3 \text{ requires } C = 60.0, H = 5.71 \text{ per cent.}$$

This compound, like the ethyl salt, gave no coloration with ferric chloride and formed no copper salt. Its aqueous solution had an acid reaction, and gave the lactone on boiling.

The properties of these two compounds suggested that the acidity of the methyl and ethyl esters of dehydracetic acid might also be due to hydrolysis in aqueous solution. Specimens of these two sub-

stances were therefore prepared, and it was found that on boiling with water they were completely decomposed into dehydracetic acid and the alcohol. The former compound (m. p. 108°) crystallised out on cooling. The distillate from boiling solutions of ethyl dehydracetate or the ethyl ester of triacetic lactone was found to contain appreciable quantities of ethyl alcohol, which was recognised by applying the iodoform test.

In conclusion, I desire to express my warmest thanks to Professor Collie, at whose suggestion this research was undertaken, and who has given me every assistance throughout the course of the work.

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CXX.—*The Behaviour of the Vapours of Methyl Alcohol and Acetaldehyde with Electrical Discharges of High Frequency.*

By HERBERT JACKSON and DUDLEY NORTALL-LAURIE.

MANY experiments have been made on the behaviour of various gases and vapours under the influence of electrical discharges, but so far as we know no experiments have been published dealing directly with the first change and not with the accumulated changes which occur when such vapours as those of methyl alcohol and acetaldehyde are subjected to the rapid oscillations of a high frequency discharge.

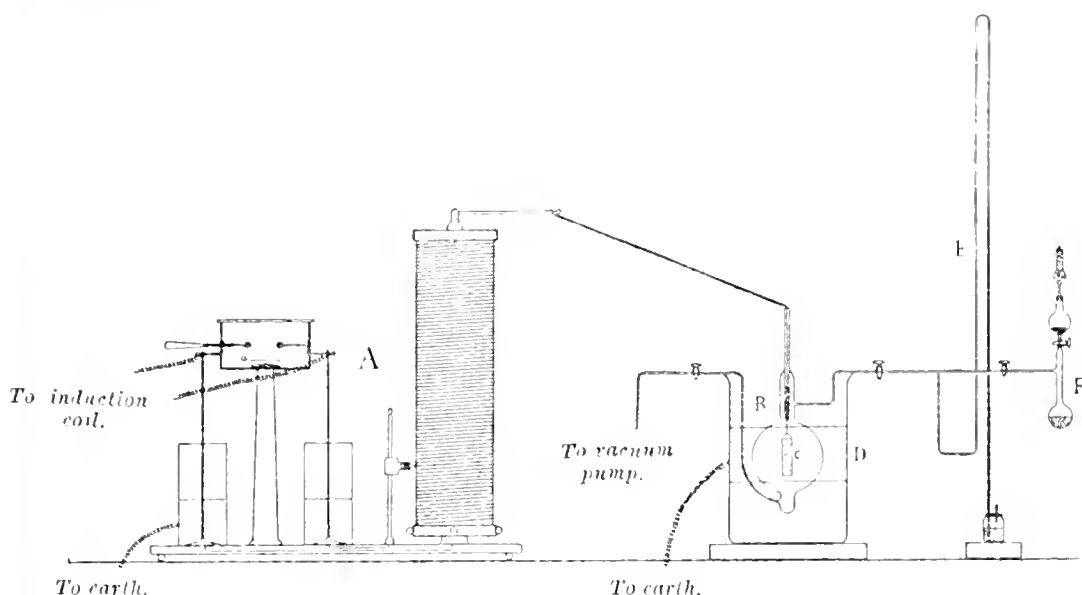
In 1901, J. N. Collie (Trans., 79, 1063) described the behaviour of carbon dioxide at low pressures when submitted to the electric discharge from an induction coil and found that the gas was rapidly decomposed to the extent of 65—70 per cent. into carbon monoxide and oxygen. The same author (Trans., 1905, 87, 1540) has described experiments on the action of the silent discharge on ethylene and on the production of complex polymerised substances as the result of this action.

Qualitative experiments on the action of electric discharges on various saturated and unsaturated compounds led one of us to the conclusion that as a general rule the former were broken down to simpler molecules, whilst the latter were converted into complex polymerised substances. In the case of methyl alcohol and acetaldehyde, it was thought worth while to study the reaction quantitatively and

to use the high frequency current for the source of oscillation, as it would be possible in this way to avoid the effect of heat to the greatest extent.

Moreover, by employing this form of current, relatively large volumes of the vapours could be used and the immediate, not the accumulated, effect on them could be studied.

The character of the apparatus used can be seen from the accompanying illustration :



A is a high frequency machine similar to those used for therapeutical purposes, and consists of two Leyden jars with spark gap, the length of which can be adjusted, and a large solenoid on a drum which can be revolved and the length of wire in use adjusted by the position of the side terminal. This enables the apparatus to be "tuned" to give the best results with the current and size of bulb used. One jar is connected to earth, and the two jars are connected on the inside with the secondary poles of a large induction coil capable of giving a spark of 50 cm. in length in air, and on the outside, with each end of the solenoid. A current of 2 amperes at 100 volts was used in the primary coil. It is worth while noting in connection with the use of the apparatus the employment of a small vessel, "*a*," containing soda-lime inside the spark gap box, which allows of the apparatus being used for a very much longer time than when this precaution is not taken. Otherwise the acids formed by the jar spark rapidly accumulate and render the sides of the glass box conductors.

B shows the form of bulb in which the decompositions took place. It was about 12 cm. in diameter, with two side tubes joined in the manner shown. The platinum electrode is shown at *C*, and was made about 6 cm. long and 1.5 cm. in diameter, shaped like a small nutmeg

grater. The pierced and roughened surface assisted in spreading the discharge.

The bulb was hung freely inside the large beaker *D*, round the outside of which was fixed a strip of tin foil 7 cm. wide, connected to earth. The action of the tin foil caused the discharge from the electrode *C* to spread all round and completely fill the bulb with a glow. The purified and dried liquid required was contained in the bulb *F*.

E represents the mercury gauge to indicate the pressure in the apparatus. The vacuum pump was conveniently arranged for the rapid exhaustion of the bulb *B* and collection of the gases formed.

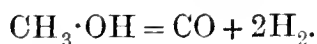
Preliminary experiments and a number of analyses of the gaseous products showed that if these were allowed to accumulate by continuing the discharge for any length of time the results obtained showed such variety as to be of little value for interpretation. If, however, the discharge were passed for a few seconds only comparable results could be obtained. The vapours were under a pressure of about 100 mm. for methyl alcohol and 180 mm. for acetaldehyde and the discharge passed for from one to ten seconds. The products were then pumped out of the apparatus, separated from the vapours, and analysed. Working in this way no solid or heavy liquid products were obtained, although these were observed if the discharge were continued for a long time.

Several analyses were made of the gaseous products obtained in this way, and it was found that the shorter the time the current was allowed to pass, the more nearly did the composition of the products (from methyl alcohol) approximate to carbon monoxide and hydrogen, the volume of the hydrogen being very nearly double that of the carbon monoxide. By working with mere flashes of the discharge and pumping out the products after each flash, gases were obtained which, when freed from the vapour of methyl alcohol and traces of water, gave the following results as the mean of several determinations of the main products:

CO.	H.	CH ₄ .	C ₂ H ₂ .	C ₂ H ₄ .
32.5	61.1	2.4	1.2	0.6

(Percentage by volume.)

We conclude that the immediate action on the vapour of methyl alcohol of such oscillations as are obtained in high frequency discharges is represented by the simple change



In the case of acetaldehyde a double reaction apparently takes place. Analyses of many samples of the gaseous products showed the presence of methane, carbon monoxide, and acetylene in large quanti-

ties, together with a very little hydrogen and other hydrocarbons. The proportions of these gases varied somewhat, but by working with discharges of very short duration it was possible to prove that the vapour of acetaldehyde decomposed partly into carbon monoxide and methane and partly into acetylene and water.

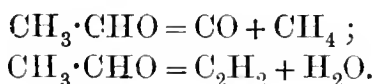
The average composition of the gas freed from water and the vapour of aldehyde and obtained with discharges of short duration is shown by the following numbers :

CO.	CH ₄ .	C ₂ H ₂ .	H ₂ .
45·2	44·2	8·6	0·4
(Percentage by volume.)			

The presence of water as one of the products was ascertained in each experiment, but it was found difficult to obtain concordant results for the small amounts formed. From these numbers it will be seen that about 80 per cent. of the vapour of the acetaldehyde yielded carbon monoxide and methane, whilst the remainder was converted into acetylene and water. The changes took place apparently simultaneously and were the primary reactions, whilst the formation of any hydrogen and other hydrocarbons was probably due to secondary changes, as the amounts of these gases only became appreciable when the discharge was continued for a minute or two. A relatively considerable quantity of the main products was obtained by a mere flash of the discharge.

The reaction giving rise to acetylene and water is apparently a reversible one, as when steam and acetylene were subjected to the discharge it was found possible by quickly removing the products to detect an aldehyde readily and to prove that it was acetaldehyde. An aldehyde was also obtained from carbon monoxide and methane treated similarly, but the quantity was small and there was certainly some formaldehyde produced. It is possible that the greater readiness of acetylene and water to form aldehyde may well account for the observed fact that the proportion of acetylene and water to carbon monoxide and methane was greater the shorter the duration of the discharge.

We conclude therefore that the immediate action of high frequency discharges on the vapour of acetaldehyde is represented by the equations :



CXXI.—*The Alkylation of Rhamnose.*

By THOMAS PURDIE, F.R.S., and CHARLES ROBERT YOUNG, B.Sc.

In previous communications on the alkylation of sugars by dry silver oxide and alkyl iodide (Trans., 1903, **83**, 1021, and succeeding papers), methylated derivatives of glucose, galactose, mannose, and sucrose have been described. The present paper deals with the products of the methylation of acetone- and methyl-rhamnosides, namely, dimethyl acetonerhamnoside and trimethyl methylrhamnoside, and with the dimethyl and trimethyl rhamnosides obtained from these compounds by hydrolysis. Anhydrous rhamnose being required for our work, the opportunity was taken of revising some of the divergent and perplexing observations recorded by various authors on the preparation and properties of the dry sugar.

The melting point ($86-88^{\circ}$) and permanent specific rotation in water ($[\alpha]_D^{20} + 9.06^{\circ}$) of the hydrated rhamnose used as the starting point of our preparations agreed closely with the values recorded by Tanret (*Bull. Soc. chim.*, 1896, **15**, 195), namely, $87-88^{\circ}$ and $+9.1^{\circ}$. The varying values given by Tanret, Fischer, and others for the melting point and rotatory power of anhydrous rhamnose (see Lippmann's *Chemie der Zuckerarten*) are explicable on the theory now accepted by Tanret himself (*Bull. Soc. chim.*, 1905, [iii], **33**, 337), and by other workers in this field, that the reducing sugars are capable of existing in two isodynamic forms, the α - and β -forms of Lowry (Trans., 1899, **75**, 213), which, when brought into the liquid state, undergo interconversion until an equilibrium is reached. The common crystalline rhamnose is stable at the ordinary temperature; on the analogy of glucose and for reasons given later, it is to be regarded as the hydrated α -form. It is levorotatory in a freshly-made aqueous solution, but owing to partial conversion into the dextrorotatory β -form the rotation of the solution changes rapidly, and finally assumes a constant value, $+9.1^{\circ}$. The α -form has not yet been obtained in the anhydrous state. α -Rhamnose cannot be dehydrated by heat without partial conversion into the β -form, this change occurring not only in the melted state, but even when the heating is so regulated that the substance does not fuse. Attempts to prepare pure anhydrous α -rhamnose by prolonged heating of the hydrated variety at 70° , and finally at 90° , in an exhausted flask connected with a vessel containing calcium chloride or phosphorus pentoxide, were unsuccessful. Analysis showed that the dehydration of the sugar was incomplete, whilst the rise of the melting point to 105° , and the initial dextrorotation of its aqueous solution, indicated that the change $\alpha \rightarrow \beta$ had already proceeded to a considerable extent.

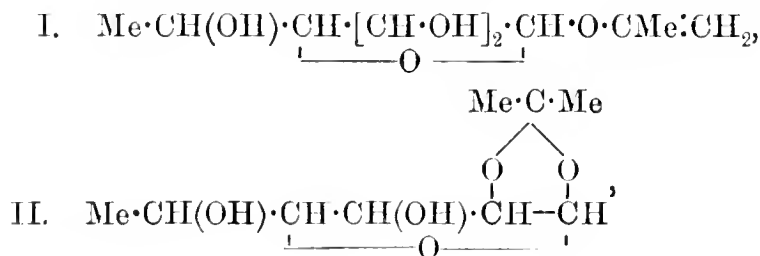
The crystalline anhydrous rhamnose of Fischer (m. p. $122-126^{\circ}$; initial $[\alpha]_D^{20} + 31.5^{\circ}$; *Ber.*, 1895, 28, 1162; 1896, 29, 324), obtained from ordinary rhamnose by repeated heating on a water-bath and crystallisation from acetone, is the β -form of the sugar. Tanret's γ -form (m. p. 110° ; initial $[\alpha]_D + 22.8^{\circ}$; *Bull. Soc. chim.*, 1896, 15, 195, 547) is doubtless the same substance mixed with some α -rhamnose. Tanret on repeating Fischer's experiments failed to obtain his high values for the melting point and initial specific rotation. We therefore repeated Fischer's experiments. After crystallising the dehydrated rhamnose three times from acetone, each crystallisation being followed by a day's heating in a steam oven, the crystalline sugar melted at $121-123^{\circ}$ and showed the initial specific rotation $+28.08^{\circ}$.

By a slight modification of the process, better results were obtained more expeditiously. The dehydrated sugar was brought into solution by prolonged boiling with thirty times its weight of dry acetone, to which about a ninth of its bulk of alcohol was added. On cooling, the sugar separated more slowly than from pure acetone, with the result that a single crystallisation and subsequent heating sufficed to raise the melting point to $122-124^{\circ}$, and the initial specific rotation in water to $+30.19^{\circ}$. Fischer's results are thus confirmed. The true solubility of β -rhamnose in acetone being small, the efficiency of the modified process is probably attributable to the slow crystallisation promoting complete isomeric change in the direction $\alpha \rightarrow \beta$. In applying Fischer's process, we found that each crystallisation from pure acetone, contrary to expectation, caused a fall of the melting point and initial rotation. The quicker crystallisation which occurs when this solvent is used yields a mixture containing more of the α -constituent than was contained in the sugar before solution. On the other hand, each subsequent heating of the solid sugar increases the proportion of the β -isomeride, and from this it may be concluded that the β -form is the form stable at higher temperatures. This conclusion is confirmed by the observation that the pure β -rhamnose referred to above, after being kept for two months in a sealed tube, gave a lower melting point ($113-115^{\circ}$) and lower initial rotation ($+25.0^{\circ}$) than when freshly prepared. The change $\beta \rightarrow \alpha$ had partially proceeded, showing that α -rhamnose is the form which is stable at the ordinary temperature.

In preparing acetonerrhamnoside, Fischer's directions (*Ber.*, 1895, 28, 1145) were carefully observed, but we failed, notwithstanding, to obtain the substance in a crystalline form. The product used in our experiments was an almost colourless syrup, devoid of action on Fehling's solution, and giving in aqueous solution the rotation $[\alpha]_D^{17} 16.04^{\circ}$, a value not differing much from that of Fischer's

crystalline substance (17.5°). If acetonerrhamnoside is capable of existing in two stereoisomeric forms, the syrup consisted essentially of the same isomeride or mixture of isomerides as Fischer's solid compound. By methylation with dry silver oxide and methyl iodide, the syrup gave a liquid levorotatory dimethyl acetonerrhamnoside, and from this, by hydrolysis with hydrochloric acid, dimethyl rhamnose was prepared. The sugar was an uncrystallisable syrup, and, as the nature of the compound appeared to prohibit its purification by distillation, it was not obtained in a state fit for analysis. The compound was, however, identified by preparation of a crystalline phenylhydrazone. Dimethyl rhamnose appears incapable of forming an osazone. When the hydrazone was heated with phenylhydrazine in alcoholic solution in a sealed tube at 100° , it was found not to be affected. Direct action of excess of phenylhydrazine acetate on an aqueous solution of the sugar also failed to give an osazone. We conclude, therefore, that in dimethyl rhamnose, and hence also in dimethyl acetonerrhamnoside, one of the two methoxyl groups is probably in the α -position. That the dimethyl rhamnose, obtained as above, had the constitution of an ordinary reducing sugar was further evidenced by its vigorous action on Fehling's solution and by its ready condensation with methyl alcohol by means of hydrogen chloride. The available quantity of the crystalline condensation product so obtained was too small to admit of satisfactory analysis, but its glucosidic nature and high levorotatory power accorded with the conclusion that it was *α -dimethyl methyl-rhamnoside*.

Considerable uncertainty prevails with respect to the constitution of the compounds of sugars with ketones. Our experiments with acetone-rhamnoside, though they do not afford conclusive proof of the constitution of the compound, at least reduce the number of possible structural formulæ that may be assigned to it. Of the two formulæ :



suggested tentatively by Fischer (*loc. cit.*), I is excluded, seeing that acetonerrhamnoside, under an action which in similar cases effects complete methylation of hydroxyl groups, yields only a dimethyl derivative. The glucosidic character of acetonerrhamnoside indicates clearly that one of the linkings of the acetone residue must be attached to the terminal C atom as in II. It is, however, improbable that the second

enzymes. As, however, various aldoses and ketoses are entirely proof against hydrolysis by all the common enzymes, it is doubtful how far these agents can be used for discriminating between the two classes of glucosidic derivatives in the case of sugars other than glucose and galactose. The method is evidently applicable to the methylmannosides, as Fischer surmised (*Ber.*, 1895, 28, 1430). α -Methylmannoside is left untouched by maltase and is scarcely affected by emulsin. β -Methylmannoside is still unknown, but observations made here (*Trans.*, 1905, 87, 1462) show that its tetramethylated derivative is readily hydrolysed by the latter enzyme. Besides this varying behaviour towards enzymes, other characteristics are available as distinguishing marks of the two classes of stereoisomerides. W. A. van Eckenstein (*Rec. trav. chim.*, 1894, 13, 183) and E. F. Armstrong (*Proc. Roy. Soc.*, 1904, 74, 188) have shown that β -methylglucoside and galactoside are hydrolysed by dilute acids much more quickly than their α -isomerides. We have found the same to hold true for the corresponding derivatives of tetramethylated glucose, galactose, and mannose, and it may be concluded that the distinction in question is a general one. Another practical method of distinction is based on the observation that Fischer's method of preparation, owing to the transforming action of alcoholic hydrogen chloride on the β -forms, furnishes the α -forms in preponderating quantity. The crystalline aldoses which separate first from the final product of the reaction are α -aldoses. On the other hand, the β -aldoses predominate in the mixture produced by alkylating methylated aldoses with silver oxide and methyl iodide. Applying the above criteria to the glucosidic derivatives of rhamnose given in the table, Fischer's crystalline methylrhamnoside, considering its method of preparation, is to be assigned to the α -series. The crystalline dimethyl methylrhamnoside obtained from dimethyl rhamnose by direct condensation is doubtless also an α -form. The syrupy methylrhamnoside used in our experiments, which was similarly obtained from rhamnose, must have been chiefly in the α -form, and the same is therefore true of the trimethyl methylrhamnoside (specific rotation -54.13° in alcohol) which was prepared from it. This was confirmed by following the course of its hydrolysis by dilute acid polarimetrically, as described in the experimental part of the paper. On the other hand, the trimethyl methylrhamnoside showing in alcohol the specific rotation $+29.30^\circ$, obtained from trimethyl rhamnose by the silver oxide and methyl iodide process, should contain a large proportion of the β -form of the compound; this was verified by the changes of rotation recorded below, which were observed during its hydrolysis by acid.

E. F. Armstrong (*Trans.*, 1903, 83, 1306) has correlated the α - and β methylglucosides with α - and β -glucose (Tammann's α - and γ -forms).

In default of similar experimental evidence in the case of rhamnose, it may be assumed on the analogy of glucose that the form of the sugar stable at the ordinary temperature, the α -rhamnose of Tanret, corresponds with the α -rhamnosides, and that Tanret's γ -rhamnose is similarly related to the β -rhamnosides. Keeping in view that rhamnose—in respect of its relationship in configuration to *l*-mannose or *l*-gulose—must be regarded as *l*-rhamnose, the tabulated rotatory powers will be seen to fall into line generally with those of glucose and its corresponding derivatives. Thus α -rhamnose is more levorotatory than β -rhamnose, α -methylrhamnoside considerably more so than α -rhamnose, whilst the rotatory powers of trimethyl α - and β -methylrhamnosides are respectively higher and lower in the *l*evo sense than that of trimethyl rhamnose.

The permanent specific rotations recorded for this sugar in water, benzene, and alcohol are the rotations of equilibrium mixtures of the α - and β -forms; the sugar being uncrystallisable, these forms cannot be isolated, but it may be safely concluded that their individual rotatory powers are respectively greater and less in the *l*evo sense than the numbers recorded for the mixture. The very slight multirotation displayed by the aqueous solution shows that the isodynamic equilibrium in the pure liquid substance and in water is nearly the same. Benzene as compared with water not only greatly lowers the initial dextro-rotation, but also affects the equilibrium, the multirotation indicating that the β -form is increased in this solvent. The direction of the multirotation both in water and in benzene is the same as that of α -rhamnose in water.

The multirotation of trimethyl rhamnose in alcohol, it will be seen, is in the opposite direction to that displayed in the other solvents, an increase in the proportion of the α -form being indicated in this case. The behaviour of the substance in alcohol is, however, quite in accord with the observations of Tanret on a similar mixture of the α - and β -forms of the parent sugar. The rhamnose (Tanret's β -variety), which gives at once a permanent dextro-rotation ($+10.1^\circ$) in water, shows multirotation in alcohol from a dextro value to -10.3° . In the case of both sugars, alcohol, as compared with water, has the effect of shifting the equilibrium in the direction $\beta \rightarrow \alpha$. Independently, however, of its influence on the isodynamic equilibrium, alcohol, like benzene, exerts a specific effect on the rotation in the *l*evo direction. Thus, even the trimethyl α - and β -methylrhamnosides, which can undergo no isodynamic change on being dissolved in alcohol, show nevertheless a much higher rotation in the *l*evo sense in alcohol than in water.

EXPERIMENTAL.

Dimethyl Acetonerhamnoside.

The proportions of materials used for the methylation were 1 mol. of acetonerhamnoside, 4 mols. of methyl iodide, and 2 mols. of silver oxide. In the first alkylation, a little acetone was added to effect solution, but in the second treatment, which sufficed to complete the action, no extraneous solvent was needed. The process of alkylation and the isolation of the product were carried out as in previous cases (*Trans.*, 1904, 85, 1058, 1074). The yield of the pure substance was approximately 35 per cent. of the weight of acetonerhamnoside taken. Dimethyl acetonerhamnoside is a colourless, mobile, highly refractive liquid, boiling at 121—124° under 22 mm. pressure. It is readily soluble in organic solvents, but insoluble in water, and it is without action on Fehling's solution.

C = 56.53 ; H = 8.75 ; OCH_3 (by Zeisel's method) = 27.36.
 $\text{C}_9\text{H}_{14}\text{O}_3(\text{OCH}_3)_2$ requires C = 56.85 ; H = 8.70 ; OCH_3 = 26.73 per cent.

A cryoscopic determination of the molecular weight in benzene gave 219, the calculated number being 232. Determinations of the specific rotation gave the following results :

	<i>p.</i>	d^{20}_D .	<i>l.</i>	α^{20}_D .	$[\alpha]^{20}_D$.
Pure liquid	—	1.0795	1	−36.09°	−33.43°
Methyl-alcoholic solution...	11.0260	0.8194	2	−5.62	−31.10
*Acetone solution	12.4781	0.8202	2	−7.23	−35.32

Dimethyl Rhamnose.

Dimethyl acetonerhamnoside was readily hydrolysed by heating at 100° with 3 per cent. aqueous hydrochloric acid, acetone being evolved in the process. The solution having been neutralised with barium carbonate, filtered, and evaporated to dryness, the product was extracted from the residue with boiling alcohol. The syrup left on evaporating the alcohol was extracted with acetone, and the solution was dried with sodium sulphate. After removing the acetone by distillation, the sugar remained as an amber-coloured, uncrystallisable syrup, solidifying to a glass after being heated on a water-bath. The substance was soluble in water and in alcohol, moderately so in acetone, only slightly so in ether. It reduced Fehling's solution on gentle warming, and was found to be feebly dextrorotatory in methyl-alcoholic solution. As the compound could not be purified for analysis, it was identified by preparing its hydrazone.

* This observation of rotatory power is to be substituted for that made on a preliminary preparation of the substance (*Chem. News*, 1902, 86, 191).

Dimethyl rhamnose and phenylhydrazine react immediately in ethereal solution with precipitation of the crystalline hydrazone, but owing to the slight solubility of the sugar in ether, it was found more convenient to add the calculated quantity of the base in the form of Fischer's reagent to a concentrated aqueous solution of the sugar; in this case also the hydrazone separates at once in the crystalline state. After being washed with acetic acid, it crystallised from alcohol in colourless, glistening prisms melting at nearly the same temperature as rhamnose phenylhydrazone, namely, 159—160°.* Analysis gave :

C = 58.59 ; H = 7.80 ; N = 10.15.

$C_{14}H_{22}O_4N_2$ requires C = 59.51 ; H = 7.87 ; N = 9.95 per cent.

The condensation of dimethyl rhamnose with methyl alcohol was carried out by heating a 10 per cent. solution of the sugar in methyl alcohol containing 0.25 per cent. of hydrogen chloride in a sealed tube for thirty hours at 90°. During the process, the observed rotation in a 1-dm. tube changed from +0.77° to -5.42°. The product, isolated as in other similar cases (*loc. cit.*), was a colourless liquid, without action on Fehling's solution, which boiled at 158—161° under 19 mm. pressure and crystallised partially on standing. The solid matter after drying on porous porcelain and recrystallising from light petroleum consisted of colourless needles melting at 53—56°, and having a specific rotation of about -95° in alcoholic solution. The glucosidic character of the compound and its high levorotatory power lead us to conclude that it is dimethyl α -methylrhamnoside.

Trimethyl Methylrhamnoside.

In methylating methylrhamnoside the materials used were in the proportions : methylrhamnoside 1 mol., silver oxide 3 mols., methyl iodide 6 mols. A few c.c. of methyl alcohol were added as solvent in the first alkylation, but although the product from this was freely soluble in methyl iodide, two additional alkylations in this solvent were needed to complete the action. By the methods described in other cases (*loc. cit.*), trimethyl methylrhamnoside was isolated from the product of the alkylation as a colourless liquid boiling steadily at 112° under 11 mm. pressure. In one experiment, 27 grams of the substance were obtained from 48 grams of methylrhamnoside. Analysis gave :

I. C = 54.68 ; H = 9.37 ; OCH_3 = 54.96.

II. C = 54.53 ; H = 9.21 ; OCH_3 = 55.73.

$C_6H_5O(OCH_3)_4$ requires C = 54.49 ; H = 9.17 ; OCH_3 = 56.37 per cent.

* The melting point of rhamnose phenylhydrazone is variously given as 159°, 154—156°, and 151°. A specimen prepared and recrystallised in the same manner as our dimethyl rhamnosephenylhydrazone melted at 150—152.5°.

A cryoscopic determination of the molecular weight in benzene gave 208. $C_{10}H_{20}O_5$ requires 220.

Trimethyl methylrhamnoside has a "bitter-sweet" taste, is neutral in reaction, and does not act on Fehling's solution; it is readily soluble in water and in the ordinary organic solvents. An aqueous solution of the rhamnoside, after being heated with emulsin at 37° for several days, showed only a slight action on Fehling's solution, and its optical rotation was unaltered. The following observations of the specific rotation were made:

	p .	d^{20° .	l .	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.
Pure liquid	—	1.0724	1	-66.68°	-62.18°
Aqueous solution.....	10.6651	1.0137	2	-3.36	-15.54
Ethyl-alcoholic solution.....	13.6455	0.8218	2	-12.14	-54.13

Trimethyl Rhamnose.

A 7.5 per cent. solution of trimethyl methylrhamnoside in 8 per cent. aqueous hydrochloric acid was heated at 100° until the constancy of the rotatory power gave proof that the hydrolysis was complete. In one such experiment the observed rotation, initially -0.83° in a 1-dm. tube, rose after two and a half hours to the constant value $+1.39^\circ$. The rise of rotation during hydrolysis was perfectly regular, a result which confirms our previous conclusion that the trimethyl methylrhamnoside consisted mostly of the α -form. The product was isolated in the same manner as tetramethyl glucose (*loc. cit.*) and distilled fractionally in a vacuum. The yield of pure product was 65 per cent. of the theoretical quantity. Analysis of the main fractions from two different preparations which distilled at 151 — 155° under 15 mm. pressure gave:

I. C = 52.16; H = 9.13; OCH_3 = 46.29.

II. C = 52.28; H = 8.99; OCH_3 = 45.48.

$C_6H_{12}O_5(OCH_3)_3$ requires C = 52.38; H = 8.82; OCH_3 = 45.15 per cent.

Trimethyl rhamnose is a syrupy liquid which reduces Fehling's solution vigorously. It is readily soluble in water, alcohol, benzene, and ether. Observations of the rotatory power of the compound are given below. The multi-rotation was promoted in each case by adding a trace of alkali.

Solvent.	c .	$[\alpha]_D^{18^\circ}$.	
		Initial.	Final.
Water	4.638	+24.15°	+25.44°
Benzene	5.238	+3.25	+5.82
Alcohol	4.938	-4.86	-9.52

When phenylhydrazine in diluted acetic acid is added to trimethyl rhamnose, the sugar is rapidly dissolved, and a heavy oil is afterwards precipitated which solidifies on standing some time. The solid product,

after being washed with dilute acetic acid, dried in a vacuum, and recrystallised from ether, gave on analysis the following results :

C = 61.32 ; H = 8.38 ; N = 9.66 ; $\text{OCH}_3 = 34.01$.

$\text{C}_{12}\text{H}_{15}\text{ON}_2(\text{OCH}_3)_3$ requires C = 60.74 ; H = 8.18 ; N = 9.48 ; $\text{OCH}_3 = 31.42$ per cent.

The compound is therefore *trimethyl rhamnosephenylhydrazone*. The substance is slightly soluble in water, very soluble in alcohol, and moderately so in ether, from which it crystallises in irregular, light yellow prisms melting and decomposing at $126-128^\circ$.

Methylation of Trimethyl Rhamnose.

The condensation of trimethyl rhamnose with methyl alcohol was effected by heating a 5 per cent. solution of the sugar in methyl alcohol containing 0.25 per cent. of hydrogen chloride in a sealed tube at 115° for four and a half hours. The product was isolated as in previous cases, and fractionally distilled in a vacuum. The distillate (b. p. $110-115^\circ$ under 11 mm. pressure) was a colourless, mobile oil which had no action on Fehling's solution. Analysis gave :

C = 54.07 ; H = 9.08.

$\text{C}_{10}\text{H}_{20}\text{O}_5$ requires C = 54.49 ; H = 9.17 per cent.

A determination of the specific rotatory power in water gave the following result : $c = 3.378$, $l = 1$, $\alpha_D^{15^\circ} = 0.46^\circ$; hence $[\alpha]_D^{15^\circ} = 13.62^\circ$. This number corresponds approximately with the value (-15.54°) found for the same compound prepared by methylating methyl-rhamnoside, and shows that the substance obtained as above consists largely of the α -form.

Trimethyl rhamnose can also be methylated by the silver oxide method. The process was carried out in the usual manner ; no solvent other than methyl iodide was required, and one treatment sufficed to complete the action. On distilling the product, the main fraction boiled at $120-124^\circ$ under 17 mm. pressure and gave on analysis :

C = 54.64 ; H = 9.20 ; $\text{OCH}_3 = 54.30$.

$\text{C}_6\text{H}_5\text{O}(\text{OCH}_3)_4$ requires C = 54.49 ; H = 9.17 ; $\text{OCH}_3 = 56.37$ per cent.

The following observations of the specific rotation were made in a 2-dm. tube : in ethyl alcohol, $c = 8.276$, $\alpha_D^{16^\circ} = +4.85^\circ$, $[\alpha]_D^{16^\circ} = +29.30^\circ$. In water, $c = 7.467$, $\alpha_D^{16^\circ} = +7.82^\circ$, $[\alpha]_D^{16^\circ} = +52.36^\circ$.

The substance is therefore trimethyl methylrhamnoside, containing, however, as explained in the introduction, a much larger proportion of the β -form of the rhamnoside than the product of the condensation of the sugar with methyl alcohol. This conclusion is borne out by a study of its hydrolysis. As in all the other aldoses examined, the

β -form—here dextrorotatory—undergoes more rapid hydrolysis than the levorotatory α -isomeride. The result is that the solution, initially dextrorotatory, becomes gradually levorotatory during the process, then again dextrorotatory, and finally attains a constant dextro-value. The hydrolysis was carried out by heating a solution of the rhamnoside in 8 per cent. aqueous hydrochloric acid at 80° . The polarimetric observations made during the process, in a 1-dm. tube, are given below :

Time from start.		Time from start.	
Before heating	+ 0.51°	70 minutes.....	- 0.11°
10 minutes.....	- 0.03	100 „	+ 0.15
30 „	- 0.18	160 „	+ 0.15
50 „	- 0.36		

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CXXII.—*The Alkylation of l-Arabinose.*

By THOMAS PURDIE, F.R.S., and ROBERT EVSTAFIEFF ROSE, Ph.D.

IN continuation of previous work on the alkylation of sugars, we have applied the process of methylation by means of the joint action of silver oxide and methyl iodide to Fischer's α -methylarabinoside. The three hydroxyl groups of the compound are readily etherified by this method, and on distilling the product *trimethyl α -methylarabinoside* is obtained in nearly theoretical yield. The distillate solidifies after some time, and by crystallisation from light petroleum the substance is procured in large, beautiful crystals melting at $43\text{--}45^{\circ}$. This compound is readily hydrolysed when heated with dilute hydrochloric acid, the progress of the action being manifested by a steady fall of the rotatory power to a final constant value ; the aldosidic methoxyl group only is removed by the process, and *trimethyl arabinose* is formed. When isolated and fractionally distilled, the substance was obtained as a colourless, uncrystallisable syrup, which showed the usual properties of a reducing sugar, including that of multirotation. When condensed with methyl alcohol by means of hydrogen chloride, it yielded a liquid mixture of trimethyl α - and β -methylarabinosides in which the α -isomeride was present in such quantity that it separated in crystalline form when the mixture was nucleated with this substance.

It was found that trimethyl arabinose, like the other etheric sugars,

could also be methylated with silver oxide and methyl iodide without undergoing oxidation. The product was again a mixture of the stereoisomeric aldoses, containing, however, such a large proportion of the β -form that the liquid could not be made to crystallise when nucleated with the crystalline α -form.

The specific rotations of the compounds referred to are summarised below; β -methylarabinoside, which is included in the table, has not been isolated hitherto. The compound was precipitated in the crystalline state (m. p. 115—117°) on adding ether to the residual mother liquors obtained in the preparation of the α -isomeride.

	$[\alpha]_D^{20}$ in water.	$[\alpha]_D^{20}$ in methyl alcohol.
L-Arabinose (Tanret).....	+175° \rightarrow 105°	—
α -Methylarabinoside (m. p. 169—171°).....	215·7	—
β -Methylarabinoside (m. p. 115—117°).....	73·2	—
Trimethyl α -methylarabinoside (m. p. 43—45°).	250·8	+223·1
Trimethyl methylarabinoside (liquid), largely β -form	121·9	97·8
Trimethyl arabinose (liquid), mixture of α - and β -forms	122·3 \rightarrow 127·2	98·7 \rightarrow 102·7

Fischer found that his methylarabinoside (m. p. 169—171°) was not affected either by yeast-enzymes or by emulsin (*Ber.*, 1894, 27, 2985). The isomeric arabinoside (m. p. 115—117°) is apparently also proof against the action of emulsin, as after heating it for a week at 35° with a solution of the enzyme we failed to obtain distinct evidence of hydrolysis. The selective action of enzymes is therefore at present not available as a distinguishing test for the stereoisomeric methylarabinosides. In view, however, of their method of preparation, which is precisely like that of the corresponding glucosides and galactosides, the arabinoside melting at 169—171° may unquestionably be assigned to the α -series, and the isomeride (m. p. 115—117°) to the β -series. The trimethyl methylarabinoside (m. p. 43—45°), which was obtained by methylating α -methylarabinoside, is also an α -form. Trimethyl β -methylarabinoside appears to be a liquid, and was not isolated. The substance was contained in apparently preponderating proportion in the aldosidic liquid (specific rotation in water +121·9°), which was obtained by methylating trimethyl arabinose by the silver oxide method. This conclusion is justified, independently of evidence based on the rotatory power of the liquid, by previous experience with other methylated sugars, which shows that the method of preparation employed always favours the production of the β -aldoside. The presence, in quantity, of this more hydrolysable form was also established by the rise and subsequent fall of rotation to the value for trimethyl arabinose, observed in the course of hydrolysing the liquid.

The relation of the trimethyl α - and β -methylarabinosides with respect to rotatory power is evidently the same as that of the cor-

responding methylarabinosides, the α -compounds being more dextro-rotatory and the β -compounds less so than the parent sugars. The mean of the specific rotations of the two methylglucosides and of the two tetramethyl methylglucosides is approximately the same, namely, 62.1° and 65° . If a similar relation applies to the arabinosides, which is probable, the specific rotation of trimethyl β -methylarabinoside in aqueous solution must be about 68° , and the liquid mixture referred to above must have contained about 70 per cent. of this isomeride. The specific rotations of the methylated arabinosides are considerably less in the dextro sense in alcohol than in water, resembling in this respect the methylated galactosides, and differing from the corresponding glucosides, mannosides, and rhamnosides, for which the converse holds true.

According to Lowry's explanation of multirotation (Trans., 1899, 75, 213), arabinose, like other reducing sugars, must exist in two isodynamic forms, only one of which, however, the ordinary crystalline sugar (specific rotation in water about $+175^\circ$), is as yet known. As the more dextrorotatory of the two forms, it is to be correlated with the more dextrorotatory methylarabinoside, which, on evidence independent of its rotatory power, we have already assigned to the α -series; the ordinary form of arabinose must therefore also be referred to this series. The rotatory powers of the α - and β -arabinoses and α - and β -arabinosides thus fall into line with those of the corresponding d -glucoses and d -glucosides. It must, however, be noted that if ordinary arabinose, in virtue of its configuration, is to be regarded as a derivative of l -glucose, relationships of a converse order might be expected, that is to say, α -arabinose and the α -arabinosides might be expected to be less rotatory in the dextro sense than the corresponding β -forms.

Trimethyl arabinose being a liquid, the rotatory powers quoted for it are necessarily those of mixtures of the α - and β -forms of the sugar. The α -isomeride, as in the case of the parent sugar, is the more dextro-rotatory of the two forms. It will be seen, however, that the multi-rotation is upwards, that is to say, in the opposite direction to that of α -arabinose. This is explained by the fact that, with the object of increasing the proportion of the presumably less stable β -form in the mixture, the liquid was heated and rapidly cooled immediately before the solutions were prepared. The heating had the expected effect, the multirotation being due to the reverse change $\beta \rightarrow \alpha$ occurring in the solutions.

EXPERIMENTAL.

 α - and β -Methylarabinosides.

The α -methylarabinoside used in our experiments was prepared from *l*-arabinose by Fischer's method (*Ber.*, 1895, 28, 1156); the yield of crystalline substance (m. p. 165—166°) was more than 40 per cent. of the weight of arabinose taken. The specific rotation of the compound, which does not appear to have been recorded hitherto, was found to be, for $c = 10.01$ in aqueous solution, $[\alpha]_D^{20} + 245.7^\circ$. On adding ether to the methyl-alcoholic mother liquors from which the α -arabinoside had been obtained, a further crystalline crop separated. The substance after being recrystallised from ethyl acetate formed beautiful prisms melting at 115—117°, which showed the following specific rotation in aqueous solution: $c = 8.1575$, $l = 2$, $[\alpha]_D^{20} + 11.95^\circ$; hence $[\alpha]_D^{20} + 73.24^\circ$. Analysis gave:

C = 43.78; H = 7.61.

$C_6H_{12}O_5$ requires C = 43.90; H = 7.32 per cent.

The compound is therefore β -methylarabinoside. The yield of material amounted to only about 8 per cent. of the arabinose taken.

Trimethyl α -Methylarabinoside.

This compound was obtained by methylating α -methylarabinoside in the manner described in previous papers (*Trans.*, 1904, 85, 1058); the proportions of materials used were 6 mols. of silver oxide and 12 mols. of methyl iodide to 1 mol. of arabinoside. After three alkylations, the action was complete, and the product was then isolated in the usual manner and distilled fractionally. From 28.5 grams of α -methylarabinoside there were obtained 30 grams of the trimethylated derivative in the form of a colourless liquid which boiled at 124—124.5° under 14 mm. pressure, and after some time solidified to a crystalline mass. The substance had no action on Fehling's solution; it was very soluble in water and all organic solvents except light petroleum, from which it separated in large crystals melting at 43—45°.

The results of analysis were:

C = 52.38; H = 8.86; $OCH_3 = 60.02$.

$C_5H_6O(OCH_3)_4$ requires C = 52.42; H = 8.74; $OCH_3 = 60.19$ per cent.

A cryoscopic determination of the molecular weight in benzene gave 197 instead of the calculated number 206, and determinations of the specific rotations showed the following results: in aqueous solution,

$p = 9.897$, $d^{20} = 1.0149$, $l = 2$, $\alpha_D^{20} + 50.38^\circ$; hence $[\alpha]_D^{20} + 250.78^\circ$; in methyl-alcoholic solution, $p = 12.134$, $d^{20} = 0.8253$, $l = 2$, $\alpha_D^{20} + 44.68^\circ$; hence $[\alpha]_D^{20} + 223.08^\circ$.

Trimethyl Arabinose.

The compound was prepared by hydrolysing trimethyl α -methyl-arabinoside. The process was carried out by heating a 9 per cent. solution of the substance in 8 per cent. aqueous hydrochloric acid, in the first instance at 70° and finally at 100° , until the rotatory power became constant. During the hydrolysis the observed rotation decreased steadily from $+19.83^\circ$ ($l = 1$) to the constant value $+12.98^\circ$. The specific rotation calculated from the latter number on the assumption that the arabinoside was entirely converted into trimethyl arabinose is $+153.4^\circ$; as the actual specific rotation of this compound (see below) is $+127.2^\circ$, it would appear that the hydrolysis was not quite complete. The product having been isolated in the usual manner (*loc. cit.*) and fractionally distilled, from 17.8 grams of trimethyl α -methylarabinoside taken there were obtained 9.6 grams of *trimethylarabinose* as a colourless syrup boiling at $148\text{--}152^\circ$ under 19 mm. pressure. Previous experience has shown that the alkylated sugars are more readily obtained in a pure state from the corresponding β -aldoside than from the less easily hydrolysable α -isomeride. As the results of analysis in the present instance were not quite satisfactory (C = 49.44, H = 8.37, calculation requiring C = 50.0 and H = 8.34 per cent.), the trimethyl arabinose was accordingly converted into a mixture of the α - and β -arabinosides by methylation with silver oxide and methyl iodide, as described below, and from this mixture, consisting largely of the β -isomeride, trimethyl arabinose was recovered by hydrolysis and fractional distillation. Analysis now gave:

C = 49.87; H = 8.59; $\text{OCH}_3 = 47.36$.

$\text{C}_5\text{H}_7\text{O}_2(\text{OCH}_3)_3$ requires C = 50.00; H = 8.34; $\text{OCH}_3 = 48.44$ per cent.

A cryoscopic determination of the molecular weight in water gave 174 instead of the calculated number 192. The value found in benzene, namely, 333.5, indicates the existence of associated molecules, as was also found to be the case for tetramethyl glucose in the same solvent (*loc. cit.*).

Trimethyl arabinose is a colourless syrup very soluble in water and all organic solvents, less soluble in light petroleum, from which it separates in the liquid state. It behaves in general like a reducing sugar, acting vigorously on Fehling's and ammoniacal silver solutions; it becomes yellow when heated with caustic alkali, answers to the Schiff and Molisch tests, and under the conditions described below it exhibits multirotation. A freshly-prepared methyl-alcoholic solution

of the substance, which immediately before being dissolved had been heated for an hour at 130° and then rapidly cooled, gave ($c = 7.528$ and $l = 2$) $\alpha_D^{20} + 14.86^{\circ}$; hence $[\alpha]_D^{20} + 98.69^{\circ}$. After seventy-two hours, the specific rotation had risen to the constant value 102.68° . A freshly-distilled sample gave in aqueous solution, for $c = 7.978$ and $l = 2$, $\alpha_D^{20} + 19.52^{\circ}$; hence $[\alpha]_D^{20} + 122.33^{\circ}$, which rose in one and a half hours to $+127.22^{\circ}$, this value remaining unaltered when a trace of alkali was added.

Condensation of Trimethyl Arabinose with Methyl Alcohol.

The condensation was effected by heating an 8 per cent. solution of the sugar in methyl alcohol containing 0.25 per cent. of hydrogen chloride in a sealed tube at 110° . After seven hours, the observed rotation had risen from $+6.48^{\circ}$ to $+8.50^{\circ}$ ($l = 1$) and the action on Fehling's solution had disappeared. The product, after being isolated in the usual manner and distilled (b. p. $128-134^{\circ}$ under 22 mm. pressure), crystallised partially on being nucleated with trimethyl α -methyl-arabinoside, and the crystals were identified with this compound by their melting point, $42-45^{\circ}$. The rotation of the mixture in methyl alcohol, for $c = 6.9715$ and $l = 2$, was $\alpha_D^{20} + 17.13^{\circ}$; hence $[\alpha]_D^{20} + 122.86^{\circ}$. The specific rotation, as was to be expected, is lower than that of the pure α -isomeride and higher than that of the isomeric mixture obtained by alkylation as described below.

Methylation of Trimethyl Arabinose by the Silver Oxide Reaction.

The sugar was methylated with a large excess of methyl iodide and silver oxide, and the product was isolated in the customary way and purified by distillation. From 10.3 grams of trimethyl arabinose, 8.5 grams of a mixture of the α - and β -arabinosides were obtained (b. p. $121-129^{\circ}$ under 22 mm. pressure). The distillate had only a very slight action on Fehling's solution, and gave on analysis:

C = 52.28; H = 8.81; $\text{OCH}_3 = 60.9$.

$\text{C}_5\text{H}_6\text{O}(\text{OCH}_3)_4$ requires C = 52.42; H = 8.74; $\text{OCH}_3 = 60.19$ per cent.

As in the case of the tetramethyl methylglucosides, trimethyl β -methylarabinoside boils at a somewhat lower temperature than its α -isomeride. Thus, on redistilling the mixture of arabinosides and collecting the distillate in two fractions, boiling at $128-132^{\circ}$ and at $132-136^{\circ}$ under 22 mm. pressure, it was found from observations of the rotatory powers that the lower boiling fraction contained a larger proportion of the less dextrorotatory β -form. This fraction in aqueous solution gave, for $c = 8.777$ and $l = 2$, $\alpha_D^{20} + 21.40^{\circ}$; hence $[\alpha]_D^{20} + 121.90^{\circ}$;

and in methyl-alcoholic solution for $c = 6.28$ and $l = 2$, $\alpha_D^{20} + 12.29^\circ$; hence $[\alpha]_D^{20} + 97.8^\circ$. The specific rotations of the higher boiling fraction in the same solvents and for similar concentrations were respectively $+127.35^\circ$ and $+107.64^\circ$. The presence of the α - and β -arabinosides in the mixture was confirmed by the occurrence of the characteristic rise and subsequent fall of the rotation during hydrolysis which has been observed in other similar cases. Thus a solution of the lower boiling fraction in 5 per cent. aqueous hydrochloric acid, when heated at 100° , showed the following variations of α_D^{20} for $l = 1$ and $c = 9.732$. At the beginning, $+12.13^\circ$, after ten minutes, $+13.12^\circ$, and after fifteen minutes $+11.37^\circ$, this value remaining constant on further heating. The specific rotation, calculated from the final number on the assumption that the mixture of arabinosides had been entirely converted into trimethyl arabinose, is $+125.4^\circ$. The specific rotation of the pure sugar in aqueous solution is actually $+127.2^\circ$; the hydrolysis was therefore practically complete. The hydrolysis of the higher boiling fraction of the arabinosides gave similar results.

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CXXIII.—*Saponarin, a New Glucoside, Coloured Blue with Iodine.*

By GEORGE BARGER.

THE epidermal cells of the leaves of certain flowering plants, belonging to various natural orders, have long been known to contain, dissolved in their cell sap, a substance which is coloured blue by iodine. The colour disappears on warming and returns on cooling, as is the case with starch; it is, however, not confined to well-marked grains, but extends uniformly throughout the cell as a fine blue precipitate. On this account the substance was regarded as an amorphous variety of starch by Sanio, its discoverer (*Botanische Zeitung*, 1857, 15, 420). Sanio found the substance in the leaf-epidermis of *Gagea lutea*, and showed by plasmolysis that it is confined to the cell sap. The publication of this note led Schenk to record similar observations on the closely allied genus *Ornithogalum* (*Botanische Zeitung*, 1857, 15, 497, 555). Schenk doubted whether the substance was identical with starch, because fragments of the epidermis of *Ornithogalum* leaves,

when coloured blue by iodine, lost their colour when placed in water.

The substance was next observed in a species of *Ornithogalum* by Trecul (*Bull. Soc. bot. de France*, 1858, 5, 711), and later it was studied in the same genus by Nägeli, who definitely declared against it being starch (*Beiträge zur wissenschaft. Botanik*, 1860, 2, 187). The next reference to the substance is by Kraus, who found it in *Arum* (*Botanische Mittheilungen*, Halle, 1885). A detailed account of "soluble starch" was published by the Swiss botanist Dufour (*Bull. Soc. vaud. Sci. nat.*, 1885, 21, 227). He found it in about twenty species of *Phanerogams*, but, like his predecessors, he did not isolate it.

The present work was started in 1901 in the botanical laboratory of Brussels University, at the suggestion of the late Professor L. Errera, to whose stimulating interest the author owes much, and some preliminary results were communicated at the meeting of the British Association in 1904. *Saponaria officinalis* was chosen as the source of material; this plant is relatively rich in the substance, and is grown on the continent for pharmaceutical purposes, so that large quantities were easily obtainable. The substance proved to be a glucoside, and the name *Saponarin* was suggested for it, leaving open the question of its probable identity with the "soluble starch" of other plants.

EXPERIMENTAL.

The method of isolation was as follows. Dried shoots of *Saponaria* were boiled several times with 10—20 times their weight of water for half an hour. Since the saponarin is confined to the epidermis, there is no advantage in powdering the leaves. The various decoctions were strained through linen and concentrated on the water-bath to one-quarter of their original volume; they were next acidified with acetic acid and left standing for several weeks, during which time a grey deposit was slowly formed, the saponins present hindering precipitation. The precipitate was separated, made into a thin cream with water, and poured into a hot one per cent. sodium carbonate solution (1 litre per kilogram of dry leaves), in which nearly the whole of the precipitate dissolved with a yellow colour. The alkaline solution was so dilute, that it could be acidified with acetic acid without causing any immediate precipitation (because of the presence of the saponins). Neutral lead acetate solution was then added, which produced a bulky precipitate of gums and other impurities. These were separated and the acid filtrate was left standing for several weeks in order to allow the crude saponarin to precipitate. This substance has a tendency to adhere to the sides of glass vessels. It still contained more than 30 per

cent. of impurities; the complete elimination of these was at first very difficult, for the glucoside is almost or quite insoluble in nearly all organic solvents. It could to some extent be purified by repeated solution in alkalis and precipitation by acids, when it separated in minute sphaero-crystals. The only organic solvent available was pyridine, in which it is extremely soluble on warming. On cooling, the substance does not separate out, even when a large quantity of water or alcohol is added. With ether and light petroleum, an amorphous precipitate is formed, but the following method proved eminently successful. The crude saponarin was dissolved in boiling pyridine; the dark brown solution was filtered and the filtrate was evaporated in a vacuum on the water-bath. A dark syrup remained behind, which retained traces of pyridine and was readily soluble in hot water (although the glucoside itself is insoluble in water containing pyridine). The aqueous solution was diluted, and on standing deposited isolated microscopic needles (not sphaero-crystals, as when an alkaline solution is acidified).

The needles were collected on a hardened filter paper by means of the pump and washed by suspension in hot water. When dried in the air, saponarin is a white powder; after being dried in a vacuum it becomes pale yellow. It is quite insoluble in cold water, but readily dissolves, with an intense yellow coloration, in dilute solutions of caustic alkalis and alkali carbonates, especially on warming. Hence, if boiled for some time in a glass vessel, a little is dissolved by the alkali of the glass. The glucoside is also soluble with a bright yellow colour in concentrated mineral acids, the solution in sulphuric acid showing a blue fluorescence. On acidifying an alkaline solution and on diluting a solution in concentrated acids with water, the yellow colour disappears, but the glucoside is not immediately precipitated if the solution is dilute. This power of remaining in a state of pseudo-solution is a characteristic property of saponarin, and in this condition it gives with iodine in potassium iodide the blue or violet coloration which led to its discovery. This coloration disappears on warming, but returns again on cooling, and in other respects closely resembles that produced by iodine and starch; the differences are merely quantitative, in the sense that saponarin has by far the smaller power of absorbing iodine. Accordingly the blue colour disappears completely on dilution with a little alcohol or much water, and can then be regenerated by adding starch solution. It is possible to obtain crystalline saponarin, coloured blue with iodine, by allowing a solution of the glucoside in dilute acetic acid containing a little iodine to evaporate slowly on a watch-glass. Blue needles separate out. A solution of saponarin can further be distinguished from a starch solution by the fact that it is coloured reddish-brown by ferric

chloride and bright yellow by alkalis. Normal lead acetate does not precipitate it, but basic lead acetate gives a bulky, yellow precipitate. Saponarin is almost or quite insoluble in nearly all organic solvents. It dissolves to a small extent in hot glacial acetic acid and in aniline, more readily in the chloroacetic acids, in piperidine, quinoline, and phenylhydrazine; it is very soluble in pyridine. When heated slowly, it melts and decomposes at 231—232°, but if the bath is previously heated to 230° the melting point is 236°.

The glucoside is levorotatory. A solution containing 0.924 gram in 100 c.c. of pyridine gave $\alpha_D - 0.73^\circ$ in a 1-dm tube, whence $[\alpha]_D - 7.90^\circ$.

The air-dried substance contains water of crystallisation which cannot be removed by heat alone, but which is completely expelled on standing for a week, at the ordinary temperature, in a vacuum over sulphuric acid, so that no further loss occurs when the substance is heated in a vacuum at 100°. The anhydrous substance is extremely hygroscopic; when left in the balance case for half an hour, it absorbs the whole of the water of crystallisation which it had lost. On this account some difficulty was at first experienced in analysing the anhydrous substance, and the boat had always to be weighed enclosed in a stoppered weighing bottle. The various samples were recrystallised two or three times by the pyridine-water method and dried in a vacuum.

0.1883 gave 0.3706 CO₂ and 0.0862 H₂O. C = 53.68; H = 5.09.

0.1446 „ 0.2846 CO₂ „ 0.0675 H₂O. C = 53.68; H = 5.19.

0.1192 „ 0.2358 CO₂ „ 0.0559 H₂O. C = 53.95; H = 5.22.

0.1714 „ 0.3380 CO₂ „ 0.0784 H₂O. C = 53.78; H = 5.08.

0.1465 „ 0.2898 CO₂ „ 0.0653 H₂O. C = 53.95; H = 4.95.

C₂₁H₂₄O₁₂ requires C = 53.85; H = 5.13 per cent.

The water of crystallisation in the air-dried substance was determined by drying in a vacuum until constant.

At the ordinary temperature 0.1854 lost 0.0131 H₂O. H₂O = 7.07.

„ „ „ „ 0.1580 „ 0.0115 H₂O. H₂O = 7.28.

„ „ „ „ 0.3529 „ 0.0248 H₂O. H₂O = 7.03.

At 100° 0.2553 „ 0.0181 H₂O. H₂O = 7.09.

The air-dried substance was also analysed.

1. Obtained by exposing the moist substance to the atmosphere: 0.2166 gave 0.3942 CO₂ and 0.1105 H₂O. C = 49.64; H = 5.67.

2. Obtained by exposing the anhydrous substance to the atmosphere: 0.1735 gave 0.3216 CO₂ and 0.0846 H₂O. C = 50.55; H = 5.42.

C₂₁H₂₄O₁₂·2H₂O requires H₂O = 7.14. C = 50.00; H = 5.56 per cent.

The molecular weight was determined* in pyridine solution (*a*) with the substance dried at 100° : 0.299 gram in 2.96 grams of pyridine was between 0.223 and 0.238 mol., benzil as standard, ordinary temperature, hence $M = 424\text{--}453$, mean 438; (*b*) with the substance dried in a vacuum, the pyridine dried over caustic potash: 0.209 gram in 1.98 grams pyridine was between 0.22 and 0.23 mol., benzil as standard, temperature 90° , hence $M = 459\text{--}480$, mean 469.

$C_{21}H_{24}O_{12}$ requires 468.

The lead salt was also analysed. It was prepared by precipitating a solution of the glucoside in dilute ammonia with neutral lead acetate, filtering, and washing the yellow precipitate by suspension in hot water. The lead salt was dried in a vacuum until constant in weight and completely decomposed by heating with fuming nitric acid in a sealed tube, the lead being then estimated as sulphate.

0.3489 gave 0.2444 $PbSO_4$. $Pb = 47.8$.

$C_{21}H_{20}O_{12}Pb_2$ requires $Pb = 47.2$ per cent.

Ennea-acetylsaponarin.

The glucoside is readily acetylated by boiling for a few seconds with a large excess of acetic anhydride and a few drops of concentrated sulphuric acid. The acetyl derivative is easily soluble in hot alcohol and crystallises on cooling in microscopic, curved needles, melting at $183\text{--}185^{\circ}$. It is extremely soluble in ethyl acetate, benzene, and chloroform, and was purified by dissolving in ethyl acetate, which leaves a small quantity of an impurity behind, and then crystallising from a dilute solution in alcohol; 0.915 gram in 10 c.c. of ethyl acetate gave, in a 1-cm. tube, $\alpha_D - 4.90^{\circ}$, whence $[\alpha]_D - 5.33^{\circ}$.

0.1436 gave 0.2911 CO_2 and 0.0618 H_2O . $C = 55.29$; $H = 4.78$.

0.2078 gram in 0.8586 gram of ethyl acetate was intermediate between 0.2875 and 0.300 mol. benzil.

Hence $M = 807\text{--}842$, mean = 825.

$C_{21}H_{15}O_{12}(C_2H_3O)_9$ requires $C = 55.32$; $H = 4.96$ per cent. $M = 846$.

The number of acetyl groups was determined by A. G. Perkin's ethyl acetate method (Trans., 1905, **87**, 107).

1. 0.4246 gram gave 0.2748 gram acetic acid = 64.8.

2. 0.7223 ,, ,, 0.4632 ,, ,, ,, = 64.1.

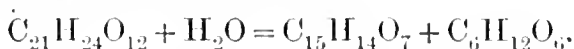
Theory for nine acetyl groups requires 63.8 per cent.

* All molecular weight determinations in this paper were made by the author's microscopic method (Trans., 1904, **85**, 286; 1905, **87**, 1756).

Acetyl-saponarin does not give a blue coloration with iodine, neither is it coloured by alkalis or ferric chloride. When boiled with acids in alcoholic solution, the acetyl groups are not only eliminated, but the glucoside itself is hydrolysed. Saponarin was, however, easily recovered by pouring the alcoholic solution of the acetyl compound into hot dilute caustic soda solution, which was kept stirred. The acetyl compound is thus precipitated in a finely-divided condition and at once undergoes saponification, the glucoside dissolving with a yellow colour. On acidifying, the saponarin is precipitated, and on recrystallisation from pyridine and water is found to be identical with the purest saponarin previously obtained, melting at exactly the same temperature.

Hydrolysis of Saponarin; Formation of Viterin and Saponaretin.

When saponarin is boiled with dilute mineral acids it is slowly hydrolysed according to the equation :



A sugar is formed which reduces Fehling's solution and gives an osazone melting at 205°. This osazone, after recrystallisation from alcohol, was mixed with an equal quantity of pure glucosazone, and the melting points of the mixture and of both constituents were determined simultaneously and found to be identical. The sugar is therefore glucose. In accordance with its glucosidic nature, saponarin gives Molisch's furfuraldehyde reaction with sulphuric acid and α -naphthol or thymol.

An estimation (by Fehling's solution) of the amount of sugar produced did not yield a very satisfactory result. As usual in such cases, it fell considerably short of the theoretical quantity.

1.2692 gram saponarin, dried in a vacuum, gave on hydrolysis 0.4253 gram glucose = 33.5.

$\text{C}_{21}\text{H}_{24}\text{O}_{12}$ requires glucose = 38.5 per cent.

The isolation of the phenolic product of the hydrolysis was attended with much difficulty, as it appeared for the most part as an uncrystallisable resin, however much the conditions were varied. The best results were obtained by boiling 10 grams of the glucoside for sixteen hours with 200 c.c. of 2 per cent. sulphuric acid. The saponarin was slowly dissolved, forming a dark yellow solution, which at first still gave the blue coloration with iodine. When this reaction was no longer obtained, a small quantity of a black, resinous decomposition product was separated and the solution was cooled. Only drops appeared and, on standing for some hours, collected at the bottom of

the flask as a viscid, brown mass. The aqueous solution was decanted and the brown syrup dissolved in a little absolute alcohol. On standing, the alcoholic solution deposited a small quantity of a crystalline substance, which was ultimately found to be identical with vitexin, a colouring matter obtained by A. G. Perkin from the dye-wood of the New Zealand tree *Vitex littoralis* (Trans., 1898, **73**, 1030; and 1900, **77**, 416).

After decantation, the sulphuric acid in the aqueous solution was precipitated with baryta. On separating the barium sulphate, the solution was found to be dark yellow, owing to a very slight excess of baryta having been employed, which formed a salt of the colouring matter, but left the solution neutral to litmus. On boiling, this solution also deposited a quantity of vitexin, which at first separated in isolated characteristic leaflets, as from the alcoholic solution already referred to. Later, groups of such leaflets and sphaero-crystals were formed, of a much darker (brown) colour. The highest yield of vitexin obtained in several experiments only amounted to 13 per cent. of the theoretical. It was often much lower, and this poor yield suggested that vitexin was present as, or derived from, an impurity in the saponarin employed. Accordingly 1 gram of a sample of the glucoside, which had been purified for analysis by two crystallisations from pyridine water and consisted entirely of isolated needles, was hydrolysed with 2 per cent. sulphuric acid. This sample also yielded more than 10 per cent. of vitexin, so that the latter substance is undoubtedly a product of the hydrolysis of saponarin.

The rest of the glucoside had been converted into another amorphous substance, which remained dissolved in the alcohol, and may be called *saponaretin* (in analogy to saliretin).

Often, especially if the alcohol is dilute, some of the saponaretin was eventually deposited along with the vitexin as a spongy, yellow mass. A separation can, however, be readily effected by means of boiling alcohol, which dissolves the amorphous saponaretin and leaves the crystals of vitexin behind.

Vitexin (from Saponarin).

This substance crystallises in microscopic, rhomb-shaped, glistening plates of a pale yellow colour, melting at 260° with characteristic frothing. The bath was heated to 240° before the introduction of the substance. Vitexin is soluble in water, and slightly so in alcohol. Like the parent substance, saponarin, it readily dissolves in pyridine, and in dilute alkali with a golden-yellow colour. The solubility in boiling alcohol is so small that this is not a satisfactory solvent for recrystallisation. This difficulty can be overcome by acidifying an

alkaline solution in hot alcohol with acetic acid, but better results are obtained by dissolving in pyridine, adding a little water, and extracting repeatedly with light petroleum until crystallisation takes place in the aqueous layer. With ferric chloride, its alcoholic solution gives the same reddish-brown coloration as saponarin itself, but it does not give the blue coloration with iodine. The substance contains no water of crystallisation. For analysis it was dried in a steam oven, and then did not undergo a further loss of weight when dried in a vacuum at 100° .

0.1395 gave 0.3022 CO_2 and 0.0606 H_2O . $\text{C} = 59.08$; $\text{H} = 4.83$.

0.0922 „ 0.1993 CO_2 „ 0.0395 H_2O . $\text{C} = 58.95$; $\text{H} = 4.75$.

$\text{C}_{15}\text{H}_{14}\text{O}_7$ requires $\text{C} = 58.82$; $\text{H} = 4.57$ per cent.

The molecular weight was determined at the ordinary temperature in pyridine solution.

A solution of 0.0634 gram in 1.849 grams pyridine was intermediate between 0.103 and 0.1065 mole., azobenzene as standard.

Hence $M = 327$; $\text{C}_{15}\text{H}_{14}\text{O}_7$ requires 306.

Acetylvitexin.

As Perkin observed, the acetylation of vitexin proceeds best in the absence of sodium acetate ; he therefore boiled the substance with acetic anhydride for six hours. If, however, a few drops of sulphuric acid are added, the change is complete in a few seconds.

The acetyl derivative is white, difficultly soluble in hot alcohol, readily soluble in glacial acetic acid, and crystallises from the latter solvent in stout, microscopic crystals melting at $257-258^{\circ}$.

0.1533 gave 0.3256 CO_2 and 0.0648 H_2O . $\text{C} = 57.93$; $\text{H} = 4.70$.

$\text{C}_{15}\text{H}_9\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ requires $\text{C} = 58.14$; $\text{H} = 4.65$ per cent.

The molecular weight was determined in chloroform solution, using azobenzene as standard. 0.3076 gram dissolved in 3.135 grams of chloroform was intermediate between 0.18 and 0.19 mole. Hence $M = 516-545$, mean 530.

$\text{C}_{15}\text{H}_9\text{O}_7(\text{C}_2\text{H}_3\text{O})_5$ requires $M = 516$.

The number of acetyl groups was determined by Perkin's ethyl acetate method :

0.4006 gave 0.2292 acetic acid = 57.2 ;

and also by weighing the regenerated vitexin (in a Gooch crucible)

0.2040 gave 0.1194 vitexin = 58.5.

Theory for five acetyl groups requires acetic acid = 58.1 and vitexin = 59.3 per cent.

The same acetyl derivative is obtained by the use of acetyl chloride in pyridine solution.

Saponaretin.

This substance is the chief product when saponarin is hydrolysed with dilute acids. Most of it separates from the acid solution on cooling in the form of a dark yellow syrup, and can be freed from accompanying vitexin by alcohol as already described. If the alcoholic solution after separation of the vitexin is evaporated on the water-bath in a vacuum, a viscous syrup is left behind, but if this is redissolved in absolute alcohol and again evaporated, so as to remove all the water, the saponaretin can be obtained as a light yellow powder.

After most of the saponaretin has been deposited as a thick syrup from the acid solution on cooling, further quantities separate out in the course of a few days as a pale yellow solid, which consists of minute, sphaero-crystals embedded in a gelatinous matrix. After filtering it can be purified by redissolving in boiling water and allowing to cool, when it separates again in the same form, without ever assuming a definitely crystalline form. When the moist substance is heated, it melts below 100° and forms a resin. If, however, it is first dried at the ordinary temperature in a vacuum, the jelly shrinks very much and darkens. It can then be heated without melting to above 200°, and it is gradually decomposed at a higher temperature without showing a true melting-point. Saponaretin has not yet been obtained pure. From its hot aqueous solution it separates as a syrup, from a cold solution as a jelly. In alcohol it is extremely soluble, and, although crystals are formed when a concentrated solution is allowed to evaporate slowly, these crystals could not be freed from the mother liquor. Saponaretin is insoluble in most other organic solvents, and from mixtures of such solvents with alcohol it always separates as a jelly.

On acetylation, a very soluble acetyl compound is obtained which melts at a low temperature and could not be crystallised, nor could other crystalline derivatives be isolated.

In other respects the substance closely resembles vitexin, for instance, in its behaviour with alkalis and with ferric chloride.

At first it was supposed that the two substances differed by a molecule of water, but saponaretin also seems to have the formula $C_{15}H_{14}O_7$, although, as the substance was amorphous, conclusive proof is wanting. For analysis, the substance was twice allowed to separate in the gelatinous condition from water, and was then dried in air and finally in a vacuum over sulphuric acid, when it underwent a further

considerable loss of weight. As in the case of saponarin, saponaretin is very hygroscopic, so that the boat had to be weighed while enclosed in a stoppered tube.

0.2062 gave 0.4412 CO_2 and 0.0853 H_2O . $\text{C} = 58.36$; $\text{H} = 4.60$.

0.1221 „ 0.2595 CO_2 „ 0.0527 H_2O . $\text{C} = 57.97$; $\text{H} = 4.78$.

$\text{C}_{15}\text{H}_{14}\text{O}_7$ requires $\text{C} = 58.82$; $\text{H} = 4.57$ per cent.

When dried at $130\text{--}160^\circ$, the substance loses a little more water and corresponds with the formula $\text{C}_{15}\text{H}_{12}\text{O}_6, \frac{1}{2}\text{H}_2\text{O}$, but prolonged heating at this temperature decomposes saponaretin, and in no case did it approximate to the formula $\text{C}_{15}\text{H}_{12}\text{O}_6$.

It may be that saponaretin is identical with Perkin's homovitexin, to which he assigns the formula $\text{C}_{16}\text{H}_{16}\text{O}_7$ or $\text{C}_{18}\text{H}_{18}\text{O}_8$. Both substances differ from vitexin in being readily soluble in boiling alcohol; the composition of saponaretin dried at 160° approximates to that of homovitexin. Both substances yield, on fusion with caustic alkali, phloroglucinol and *p*-hydroxybenzoic acid. Both separate from the vitexin mother liquor on exposure to air as an amorphous product, but homovitexin was finally obtained by Perkin in a crystalline form.

Decomposition by Caustic Alkali.

Caustic potash (7 grams), to which a little water had been added, was melted in a nickel crucible and finely-powdered saponarin (1.6 grams) was gradually dropped in. The temperature was kept between 190° and 200° . After each addition of the glucoside, the fused mass was stirred with a platinum wire. The fused mass, which was dull red, was dissolved in water, acidified with hydrochloric acid, and extracted with ether; the ethereal solution was shaken with sodium carbonate and then evaporated. It left a minute quantity of a substance readily soluble in water, which reddened a pine wood splinter, previously dipped in hydrochloric acid; the presence of phloroglucinol was thus indicated. The sodium carbonate solution on acidification and extraction with ether gave a crystalline acid, which was recrystallised from water containing a little animal charcoal and then melted at 210° . With ferric chloride, no coloration, but a yellow precipitate, was produced. When rapidly heated, phenol was formed, and was detected by its odour and by the tribromophenol test. The substance was evidently *p*-hydroxybenzoic acid.

The quantity available was used for the determination of the water of crystallisation.

0.0574 of the air-dried crystals lost 0.0069 gram when heated to 110° . Hence $\text{H}_2\text{O} = 12.0$.

$\text{C}_7\text{H}_6\text{O}_3, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.5$ per cent.

A larger quantity of the acid was then prepared in the same way and analysed :

0.1398 gave 0.3102 CO_2 and 0.0539 H_2O . $\text{C} = 60.51$; $\text{H} = 4.28$.

$\text{C}_7\text{H}_6\text{O}_3$ requires $\text{C} = 60.87$; $\text{H} = 4.34$ per cent.

Although sufficient of the acid was thus obtained, the amount of the other substance (phloroglucinol) was too small for identification, so that experiments were next made with aqueous caustic alkali.

Several grams of saponaretin were boiled for one and a half hours with a solution containing equal parts of caustic potash and water. At the end of that time, the solution no longer became bright yellow on diluting with water. It was slightly acidified, neutralised with sodium bicarbonate, and extracted with ether. The bicarbonate solution was found to contain a little *p*-hydroxybenzoic acid. The ethereal extract left a residue, which gave a very intense crimson coloration with pine wood. This residue was recrystallised from water containing animal charcoal, and, on standing in a vacuum, needles which did not give the pine wood reaction appeared, and finally a few large, stout prisms were obtained, which effloresced, gave an intense crimson colour with pine wood and with vanillin, a bluish-violet colour with ferric chloride, and melted at 214° . Doubtless this substance was phloroglucinol. In an attempt to recrystallise the needles which accompanied the phloroglucinol, they melted in boiling water. On leaving the aqueous solution in a vacuum, stout, glassy prisms melting at 106° were obtained.

The substance was prepared in the pure state by recrystallisation from benzene ; it then melted at 108° . It was *p*-hydroxyacetophenone.

0.1108 gave 0.2860 CO_2 and 0.0575 H_2O . $\text{C} = 70.40$; $\text{H} = 5.77$.

$\text{C}_8\text{H}_8\text{O}_2$ requires $\text{C} = 70.59$; $\text{H} = 5.88$ per cent.

The substance gave with ferric chloride a brownish-violet coloration. The semicarbazone was prepared and melted at 199° ; the benzoyl derivative melted at 134° .

The *p*-hydroxybenzoic acid produced by the fusion with potash is formed by secondary decomposition of the *p*-hydroxyacetophenone.

Identity of the Vitexin from Saponaria with that from Vitex.

Mr. A. G. Perkin, who was good enough to read this paper in manuscript before the identity of the two substances was suspected, pointed out their close resemblance, and sent the author a small specimen of vitexin, the absolute purity of which he could not guarantee. The probability of the two substances being identical was at once evident from the following comparison of their properties.

<i>Vitexin.</i>	<i>Substance from Saponarin.</i>
$C_{21}H_{20}O_{10}$ or $C_{15}H_{14}O_7$, melts at 264—265°.	$C_{15}H_{14}O_7$, melts at 260°.
Prismatic or hair-like needles of a canary-yellow colour.	Pale yellow, glistening plates.
Hepta- or penta-acetyl derivative melts at 251—256°.	Penta-acetyl derivative melts at 252°, after a second crystallisation at 257—258°.

Both substances give in alcoholic solution with ferric chloride the same reddish-brown coloration, dissolve in alkali with a light yellow colour, yield on hydrolysis with caustic potash phloroglucinol and *p*-hydroxyacetophenone, are reduced by sodium amalgam to a brown solution, which turns scarlet on neutralisation, and both dissolve in sulphuric acid in the cold to a pale yellow solution, which becomes dull olive-green on heating.

The chief differences were in the formulæ assigned to the two substances, and in their crystalline form. Perkin had adopted the formula $C_{21}H_{20}O_{10}$, because he obtained from his substance tetra-nitroapigenin, and regarded vitexin as a very stable glucoside of apigenin ($C_{15}H_{10}O_5$). He did not, however, determine the molecular weight of the substance. This determination was therefore attempted with the minute specimen received from Mr. Perkin, using pyridine, the only solvent in which vitexin is readily soluble. 0.0466 gram in 0.6726 gram pyridine was intermediate between 0.24 and 0.25 mole., using benzil as standard. Hence

$$M = \frac{0.0466 \times 1000}{0.6726 \times 0.245} = 283.$$

$$\begin{array}{ll} C_{15}H_{14}O_7 \text{ requires } 306. \\ C_{21}H_{20}O_{10} \quad \quad \quad \text{,,} \quad 432. \end{array}$$

The specimen was dark yellow and crystallised in sphaerites, but it was not perfectly pure. In order to recrystallise it, a few drops of water were added to the pyridine solution used in the molecular weight determination.

As in the case of saponarin, the addition of water did not produce a precipitate, but when nearly all the pyridine had been removed by shaking with light petroleum, crystallisation began in the lower (aqueous) layer. The substance now separated in isolated, glistening leaflets which had been found to be so characteristic of the substance obtained from saponarin.

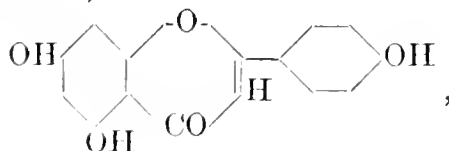
The substance was light yellow and melted at 260° when placed in the bath at 240° and rapidly heated. Vitexin, obtained from

saponarin and purified in the same way, also melted at this temperature, as did a mixture of the two substances in equal proportions. The difference from the melting point, or rather from the temperature of decomposition, given by Perkin (264—265°), is probably not due to an impurity, but to differences in manipulation, and the identity of the two substances is therefore well established.

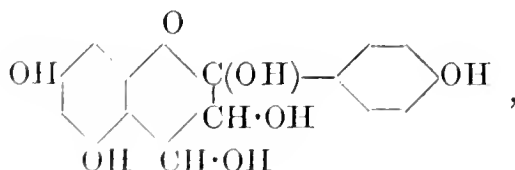
Mr. Perkin very kindly examined the tinctorial properties of the vitexin from both sources and of saponaretin. The three specimens gave similar greenish-yellow shades on woollen cloth, with chromium as mordant, and pale brown shades with iron; all three possessing only slight tinctorial properties.

Constitution of Vitexin.

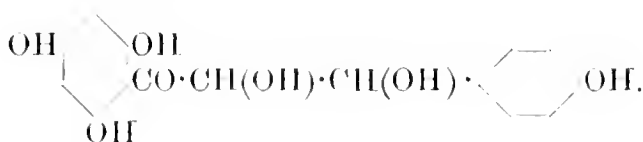
The production of phloroglucinol and *p*-hydroxyacetophenone by the action of caustic alkali, and especially the production of tetranitroapigenin by the action of nitric acid on vitexin, proved that this substance is closely related to apigenin, as Perkin pointed out (*Trans.*, 1898, 73, 1030), suggesting that it might be apigenin with a side chain attached; later (*Trans.*, 1900, 77, 422), he regarded this side chain as a sugar, and vitexin as a very stable glucoside of apigenin. The molecular weight determination of vitexin (from both sources) and of acetylvitexin, together with the production of vitexin by hydrolysis from saponarin, prove that vitexin has only the formula $C_{15}H_{14}O_7$, so that there can be no side chain. Vitexin therefore only differs from apigenin by the elements of two molecules of water. That apigenin is 1:3:4'-trihydroxyflavone,



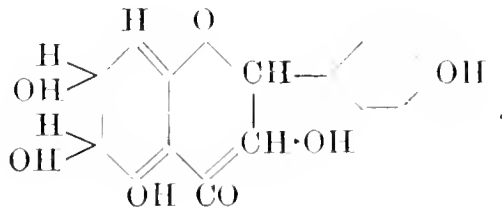
has been established by the researches of Perkin and by the synthesis due to Czajkowski, von Kostanecki, and Tambor (*Ber.*, 1900, 33, 1988). The two additional hydroxyl groups which vitexin contains are very likely not in either of the two benzene nuclei; for otherwise it is difficult to understand the fission into phloroglucinol and *p*-hydroxybenzoic acid. Hence, these two hydroxyls would appear to be in the pyrone ring or in a chain which can give rise to it (in the formation of tetranitroapigenin). This would lead to a reduced flavanone formula:



or to the corresponding reduced chalcone formula :



Both these formulæ contain six hydroxyl groups, whereas both Perkin's determinations and those of the author show that there are but five acetyl groups in acetyl vitexin. As the number of hydroxyl groups is unusually large, it may be that one escapes acetylation. Acetylsaponarin contains nine acetyl groups. Assigning to the glucose part of the molecule the structure of an α -anhydride, this would have four hydroxyl groups; the vitexin part would therefore have five, and, after hydrolysis, six, hydroxyl groups. The formation of *p*-hydroxyacetophenone from an $\alpha\beta$ -hydroxypyrone compound of the type figured would probably take place through the elimination of water, yielding the complex $\text{CH}_2:\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, the process being analogous to the formation of lævulinic acid from dextrose. Mr. Perkin has, by letter, raised objections to the above constitution for vitexin, and has suggested the presence of a reduced phloroglucinol nucleus, which would lead to a formula of the following type, with five hydroxyl groups :



The study of vitexin is complicated by the difficulty experienced, by Perkin as well as by the author, of preparing crystalline derivatives other than the acetyl compound. Numerous attempts were made to prepare a crystalline azobenzene derivative and an alkyl ether; in the former case, a resinous product was formed, and in the latter the reaction was very slow and incomplete, whether methyl iodide or dimethyl sulphate were used.

Vitexin seems to belong to a new class of colouring matters which are closely allied to the flavone group, and differ from the corresponding flavone derivatives by two molecules of water. Scoparin, which, according to Perkin, is probably methoxyvitexin, would also belong to this group.

Whether saponaretin is a chalcone derivative corresponding to vitexin, or whether it is identical with homovitexin, cannot at present be determined, nor is it known if the glucoside in *Vitex littoralis*, from which vitexin is formed by hydrolysis, is identical with saponarin.

In conclusion, the author gratefully acknowledges his indebtedness to Mr. A. G. Perkin, F.R.S., for a specimen of vitexin, for having carried out some dyeing experiments, and especially for his valuable criticism after reading this paper in manuscript.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
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CXXIV.—*The Action of Ethyl Iodide and of Propyl Iodide on the Disodium Derivative of Diacetylacetone.*

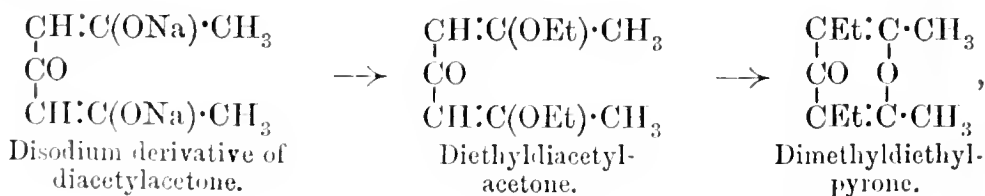
By ALEXANDER WILLIAM BAIN, B.A., B.Sc.

THE present research was undertaken with the view of determining how the basicity of dimethylpyrone would be affected by the introduction of alkyl groups into the molecule.

Collie and Steele (Trans., 1900, 77, 961) attempted to prepare tetramethylpyrone by the action of methyl iodide on the disodium derivative of diacetylacetone; the yield of this substance, however, was very small, and other substances were also obtained.

It was with the expectation that the course of the reaction would be less complex and the yields perhaps better, that the action of ethyl iodide and *n*-propyl iodide on the disodium derivative of diacetylacetone was studied.

In the case of ethyl iodide, it was anticipated that the main reaction would be similar to that by which tetramethylpyrone was obtained, and that the chief product would be dimethyldiethylpyrone, thus:



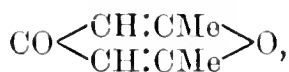
which might be expected to have similar general properties to dimethylpyrone.

In the first preparation, however, contrary to all expectation, the main product was not dimethyldiethylpyrone, but an oil which distilled without decomposition at 289° under the atmospheric pressure, and which gave none of the reactions by which dimethylpyrone is characterised. After long standing, the substance solidified to a pale yellow solid of low melting point.

On warming with sodium hydroxide, alcohol, and chloroform, it gave the orcinol reaction, namely, a deep red coloration, and the mixture on dilution with water showed a beautiful green fluorescence.

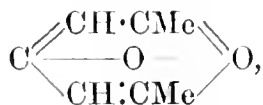
Analysis agreed with the formula $C_9H_{12}O_2$, which showed that it was isomeric with dimethylethylpyrone.

In four successive preparations, good yields of this compound were obtained, but it was only after long trial that the dimethylethylpyrone and dimethyldiethylpyrone were isolated in any considerable quantity, the conditions of experiment determining the production of this derivative on the one hand, or the mono- and di-ethyl derivatives on the other. As in the case of the compounds obtained by the action of acetyl chloride on the disodium derivative of diacetylacetone (Collie, *Trans.*, 1904, 85, 971), so in the case of the similar substances formed by the action of ethyl iodide, the formula hitherto adopted for dimethylpyrone, namely,



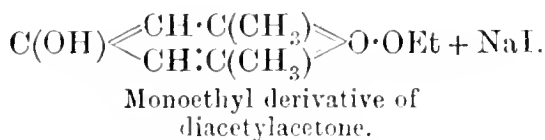
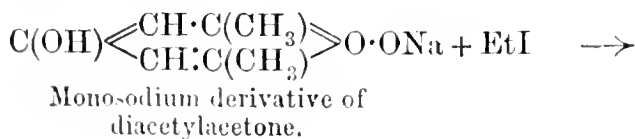
seems to be quite inadequate for the explanation of the formation of such compounds, and, indeed, is quite at variance with the properties of dimethylpyrone.

The new formula suggested by Collie (*Trans.*, 1904, 85, 971), namely,

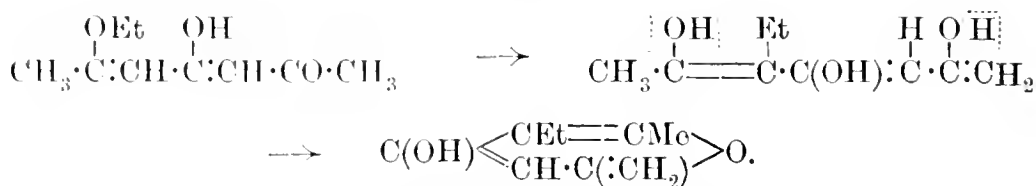


which agrees with the observed properties of this substance and accounts for its very high refractive index, makes the way clear for similar suggestions as to the formulae and the course of the reactions in the present investigation.

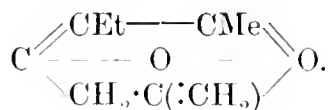
The formation of the compound isomeric with dimethylethylpyrone may be explained by the interaction of ethyl iodide and the monosodium derivative of diacetylacetone, which takes place probably thus :



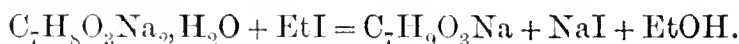
Rearrangement and subsequent loss of water take place, when we have :



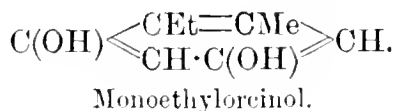
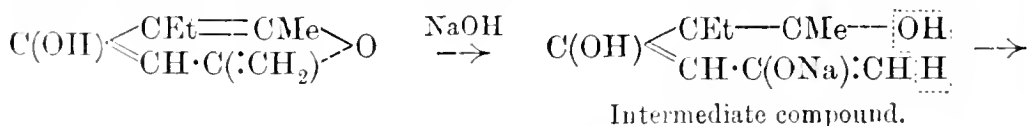
The experiments made with the substance suggest that its constitution is best represented by the tautomeric form:



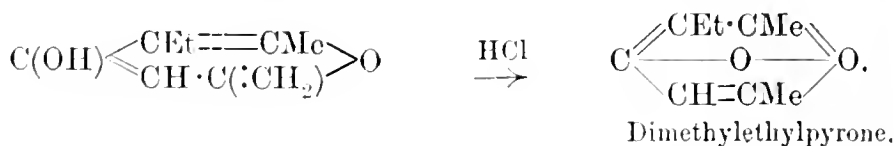
The formation of the monosodium derivative mentioned above is possibly due to the interaction of ethyl iodide on the hydrated disodium derivative of diacetylacetone. This substance, after heating on the water-bath under diminished pressure, has the composition $\text{C}_7\text{H}_8\text{O}_3\text{Na}_2, \text{H}_2\text{O}$, and it may react thus:



Also the formation of an oreinol derivative by the action of sodium hydroxide solution on the compound may be represented thus:



and, lastly, the oil, after prolonged boiling with strong hydrochloric acid, yields dimethylethylpyrone hydrochloride, thus:



The production of dimethyldiethylpyrone hydrochloride from the disodium derivative of diacetylacetone by the action of ethyl iodide may be explained in a precisely similar manner.

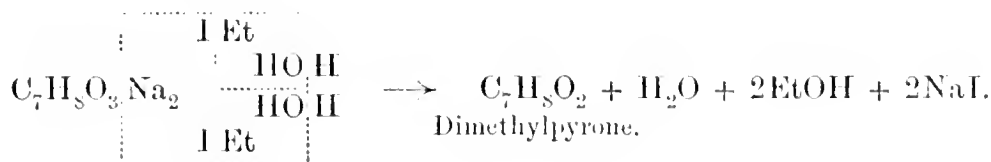
With *n*-propyl iodide also an oil was formed, which possessed properties very similar to those of the oil which was obtained by the action of ethyl iodide on the disodium derivative of diacetylacetone. The same difficulty was experienced in obtaining any dimethyl-mono- or -di-propylpyrone.

It was only after more than a year's continuous work that the true nature of these changes was discovered, the oil being obtained some-

what easily, but in varying yields, whilst hardly any pyrone derivatives were produced, and considerable quantities of dimethylpyrone itself were formed during the progress of the reaction.

The probable cause of this trouble was that in the earlier experiments the reacting substances were not quite dry, and also that the disodium derivative of diacetylacetone has the constitution $C_7H_8O_3Na_2 \cdot 2H_2O$ when prepared by precipitation from 95 per cent. alcohol.

This hydrated derivative probably reacts with ethyl iodide in the following way :



In the later experiments, this was avoided, as far as possible, by preparing pure dry diacetylacetone from the barium salt of dimethylpyrone, and the anhydrous derivative was obtained by treating this with sodium dissolved in dry alcohol (see below).

Considerable quantities of the oil were obtained by adopting this method of work, but the production of the pyrone derivatives was most disappointing until it was found that prolonged boiling with concentrated hydrochloric acid was the determining factor for a satisfactory yield.

EXPERIMENTAL.

When dimethylpyrone, prepared according to the method employed by Collie (Trans., 1891, 59, 617), is dissolved in 95 per cent. alcohol and a solution of sodium ethoxide in 95 per cent. alcohol added, a hydrated form of the disodium derivative of diacetylacetone is obtained, which is almost insoluble in boiling alcohol. This has the composition $C_7H_8O_3Na_2 \cdot 2H_2O$.

Twenty-four grams of dimethylpyrone were employed in the first experiment, and the requisite amount of sodium ethoxide for the reaction was prepared by dissolving 9 grams of sodium in 150 c.c. of ordinary absolute alcohol and then adding the dimethylpyrone, which had been previously dissolved in a little absolute alcohol. The mixture was warmed on the water-bath, when the disodium derivative of diacetylacetone separated. In the earlier experiments, this precipitate was not filtered. After several hours, 65 grams of ethyl iodide (that is, about 4 grams in excess of the calculated quantity) were added to the contents of the flask, and the whole was heated on the water-bath for nearly six hours. At the end of this time, all the suspended sodium derivative had disappeared, and the contents of the

flask had a brownish-red colour and were only faintly alkaline to litmus.

The excess of alcohol and ethyl iodide was distilled off on the water-bath, dilute hydrochloric acid was added until the contents of the flask were just acid, and the remaining traces of alcohol evaporated. The mixture was then diluted with water to dissolve the sodium iodide which had separated out, and extracted with chloroform.

The chloroform extract was dried over calcium chloride and the chloroform then removed by distillation. The residual liquid, which was somewhat viscous, was distilled under diminished pressure (35 mm.), when a small fraction was collected between 130° and 180°, but the greater part distilled at 190° as a pale yellow oil. The oil was redistilled under ordinary atmospheric pressure, when nearly 10 grams were obtained, which passed over without decomposition at a constant boiling point of 289°.

- I. 0.2000 gave 0.5189 CO₂ and 0.1472 H₂O. C = 70.7; H = 8.2.
 II. 0.1929 „ 0.4991 CO₂ „ 0.1428 H₂O. C = 70.6; H = 8.2.
 III. 0.1919 „ 0.4980 CO₂ „ 0.1404 H₂O. C = 70.8; H = 8.1.
 C₉H₁₂O₂ requires C = 71.1; H = 7.9 per cent.

A determination of the molecular weight was made by the boiling point method, the dried alcohol being used as solvent.

With 4.249 grams of solvent and 0.1535 gram of substance, a rise of 0.25° was observed, whence molecular weight = 166. The molecular weight calculated for C₉H₁₂O₂ is 152.

After standing for nearly six weeks, the substance crystallised, forming pale yellow crystals, which melted at 66—67°. It is only very sparingly soluble in water, but easily dissolves in alcohol, chloroform, and ether. It is easily soluble in acetic acid, and the acetic acid solution at once decolorises bromine water. Cold aqueous solution of potassium permanganate is instantly reduced by the substance.

The existence of the :C:CH₂ group was further confirmed by oxidising some of the compound with dilute chromic acid solution and then distilling. The distillate was strongly acid to litmus and when just neutralised with dilute sodium hydroxide solution, at once reduced ammoniacal solution of silver nitrate, thus indicating that the :CH₂ group had been oxidised to formic acid.

Ferric chloride solution gives no coloration, indicating the absence of a hydroxyl group in the molecule. Concentrated sulphuric acid produces a yellowish-red coloration, which darkens on warming. Cold sodium hydroxide solution dissolves the substance easily, giving a yellow solution which, on warming, changes to a red colour and has a fragrant smell resembling that of oil of juniper; the addition of

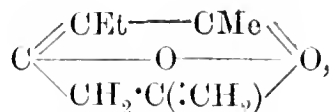
hydrochloric acid destroys the colour and odour, which, moreover, can both be destroyed by addition of excess of sodium hydroxide.

When heated with sodium hydroxide, alcohol, and chloroform, it immediately gives a deep red solution, which, on dilution with water, shows a beautiful green fluorescence, a reaction common to oreinol derivatives.

On distilling with ferric chloride solution and subsequent addition of sodium hydroxide to the distillate, a purple coloration is developed, which is discharged by hydrochloric acid and reappears on the addition of more sodium hydroxide.

The conclusion that oxygen does not appear to be doubly bound to carbon in the molecule as a carbonyl group was arrived at by the fact that all attempts to prepare an oxime, a hydrazone, and a semicarbazone failed.

The structural formula which is suggested for this compound, namely,



appears to explain the above reactions quite satisfactorily. The manner in which an oreinol derivative may be formed has already been indicated.

Lastly, on long-continued boiling with concentrated hydrochloric acid, the hydrochloride of dimethylethylpyrone was obtained (see later).

Thus, this most interesting compound possesses the remarkable property of undergoing isomeric change on being treated with acids or alkalis, resembling the diacetyl derivative isolated by Collie (*loc. cit.*).

Dimethylethylpyrone and Dimethyldiethylpyrone and their Salts.

It has already been mentioned that the earlier attempts to prepare these compounds proved a complete failure, only very small amounts of crystalline substances being extracted, which consisted chiefly of dimethylpyrone, and it was suggested that this was at all events partly due to the presence of water, which reacted in the way indicated above.

In order to eliminate as far as possible this cause of failure, all the reacting substances were very carefully dried. The disodium derivative of diacetylacetone was filtered off immediately after precipitation in absolute alcohol and heated under reduced pressure on the water-bath until free from alcohol and water. The ethyl iodide was dried over phosphorus pentoxide and redistilled, and the alcohol was boiled for several hours over lime and redistilled.

Forty grams of the carefully dried disodium derivative were suspended in 50 c.c. of the dry alcohol and 70 grams of the dry ethyl iodide (an excess of 4 grams) were added. The contents of the flask were boiled on the water-bath until the suspended substance had disappeared and the mixture was nearly neutral; this required about three hours. The alcohol and excess of ethyl iodide were removed by distillation under reduced pressure, and the residual liquid was filtered from the precipitated sodium iodide which had separated. Fifty c.c. of cold concentrated hydrochloric acid were added, and the mixture was warmed on the water-bath for two hours and then allowed to cool. By this means the alkyl derivatives of dimethylpyrone were formed as hydrochlorides. A little water was added to the mixture, which was then extracted with chloroform. By this treatment it was hoped that the whole of the oil formed would be removed, since it is extremely soluble in chloroform and is only attacked by concentrated hydrochloric acid after prolonged boiling. This was found to be the case, as after distilling off the chloroform the oil was left (b. p. 289°), but this time only a comparatively small yield was obtained (about 2 grams), the way in which the reaction had been carried out apparently not favouring its formation in quantity. The hydrochloric acid solution of the hydrochlorides was then heated on the water-bath and most of the hydrochloric acid removed by distillation. The liquid was just neutralised with solid sodium carbonate, then made just faintly acid with very dilute hydrochloric acid and extracted with ether. The ether was removed by distillation and the residue fractionated under reduced pressure (about 35 mm.). Nearly 5 grams were collected between 155° and 160° , and 4 grams between 185° and 190° . These fractions were redistilled under the ordinary atmospheric pressure, and the distillates, which passed over between 245° and 247° and 275° and 278° (about 3.5 grams and 2 grams respectively), solidified immediately on cooling.

The above method of procedure was repeated, using the same quantities, until a sufficient amount of each fraction had been obtained for examination.

Dimethylethylpyrone, $C_9H_{12}O_2$.

A portion of the compound which came over between 245° and 247° was recrystallised from water, in which it was easily soluble, and from which it separated as colourless needles. These were dried over sulphuric acid in a vacuum desiccator and then melted at 58° .

0.1945 gave 0.5081 CO_2 and 0.1383 H_2O . $C = 71.2$; $H = 7.9$.

$C_9H_{12}O_2$ requires $C = 71.1$; $H = 7.9$ per cent.

Dimethylethylpyrone in aqueous solution gives no coloration with ferric chloride. When ground with solid potassium hydroxide in a

mortar, it gives a bright pink coloration, suggesting the formation of a quinonoid compound—this colour disappears when water is added. It gives no precipitate with barium hydroxide, even when boiled with it, and its basic properties, though well marked, are not so strongly defined as those of dimethylethylpyrone itself.

The *hydrochloride*, $(C_9H_{12}O_2)_2 \cdot HCl \cdot 2H_2O$, obtained by evaporating dimethylethylpyrone with concentrated hydrochloric acid, is quite stable at the ordinary temperature, but on being heated in a test-tube loses water and hydrogen chloride. Some of the salt was prepared and dried on a porous tile. On titration with decinormal silver nitrate solution :

0.1 gram reacted with 2.6 c.c. of the silver solution, this being equivalent to 0.00923 gram chlorine. $Cl = 9.23$.

$(C_9H_{12}O_2)_2 \cdot HCl \cdot 2H_2O$ requires $Cl = 9.4$ per cent.

As already mentioned, the hydrochloride of dimethylethylpyrone is also formed from the oil which distilled at 289° by boiling it with hydrochloric acid. This transformation is only effected by boiling the oil with concentrated hydrochloric acid for at least twenty-four hours, and thus was overlooked in the earlier experiments.

Hydrochloric acid only very slowly attacks the substance, the hydrochloride of dimethylethylpyrone being obtained after evaporation of the excess of hydrochloric acid. That it was actually this compound was proved by converting it into the base by addition of sodium carbonate solution and subsequent extraction with ether, from which crystals were obtained which melted at 58° .

$C = 71.4$; $H = 7.9$. $C_9H_{12}O_2$ requires $C = 71.1$; $H = 7.9$ per cent.

The *platinichloride*, $(C_9H_{12}O_2)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, obtained by adding platinic chloride to a solution of dimethylethylpyrone in hydrochloric acid, separates out on stirring the mixture with a glass rod. This salt, which is yellow, can be recrystallised from warm water. From 1 gram of the base, nearly 0.7 gram of the recrystallised platinichloride was prepared. This was dried on a porous plate, and, after remaining for three hours in a desiccator, was analysed. That the compound prepared as described above possessed water of crystallisation was rendered evident by heating some in a test-tube, when water was driven off.

0.2150 gave 0.2261 CO_2 , 0.0086 H_2O , and 0.0556 Pt.

$C_{18}H_{30}O_6Cl_6Pt$ requires $C = 28.8$; $H = 4.0$; $Pt = 26.0$ per cent.

The ethyl derivative also gave a picrate when added to a boiling aqueous solution of picric acid. The picrate separates as an orange precipitate, but the quantity prepared was insufficient for analysis

owing to loss of material in previous unsuccessful attempts to prepare the oxalate, nitrate, and hydriodide.

Dimethyldiethylpyrone, C₁₁H₁₆O₂.

A portion of the compound which came over between 275° and 278°, after recrystallisation from alcohol, was obtained in the form of colourless crystals similar in appearance to those of the monoethyl compound. After having been dried over sulphuric acid in a vacuum desiccator, they melted at 64°.

- I. 0.1939 gave 0.5207 CO₂ and 0.1509 H₂O. C=73.2; H=8.6.
 II. 0.2170 „ 0.5825 „ „ 0.1725 „ C=73.2; H=8.8.
 III. 0.2296 „ 0.6153 „ „ 0.1825 „ C=73.1; H=8.8.
 C₁₁H₁₆O₂ requires C=73.3; H=8.9 per cent.

Dimethyldiethylpyrone gives no coloration with ferric chloride solution, neither does it form a precipitate with barium hydroxide even on boiling. Attempts to prepare an oxime and a hydrazone were made, but did not meet with success. A pink coloration was obtained when the crystals were ground with solid sodium hydroxide in a mortar, and in fact the chemical properties of this substance are almost identical with those of dimethylethylpyrone. It seems, however, to possess decidedly less basic properties than the monoethyl compound.

Repeated attempts were made to prepare salts of this compound, but, except in two instances, were unsuccessful. On adding the calculated amounts of oxalic, sulphuric, and hydriodic acids respectively to a concentrated aqueous solution of the base and allowing the mixtures to evaporate spontaneously in a desiccator, either syrupy solutions which would not crystallise resulted or the base itself crystallised out in a hydrated form.

When evaporated with concentrated hydrochloric acid, dimethyldiethylpyrone gives a hydrochloride, which separates out in colourless needles. This compound, however, is extremely unstable, and rapidly loses hydrogen chloride, even in contact with air at the ordinary temperature. No satisfactory analytical results could be obtained, although repeated attempts were made.

The *platinichloride*, (C₁₁H₁₆O₂)₂.H₂PtCl₆.2H₂O, obtained by adding excess of platinum chloride to a solution of the base in concentrated hydrochloric acid, separates as a pale brown precipitate after well shaking and stirring with a glass rod. Some of this compound was recrystallised from warm water, in which it is sparingly soluble, and dried on a porous plate.

0.2020 gave 0.2425 CO₂, 0.0870 H₂O, and 0.0489 Pt. C=32.7; H=4.8; Pt=24.2.

C₂₂H₃₂O₄.Cl₆Pt requires C=32.8; H=4.7; Pt=24.2 per cent.

This platinichloride is not nearly so stable as the corresponding platinichloride of dimethylethylpyrone, since it not only loses water on heating, but even decomposes when placed in a vacuum desiccator, losing dimethyldiethylpyrone and water.

Diethyldiacetylacetone, C₁₁H₁₈O₃.

In one of the experiments which were carried out, an attempt was made to get rid of what may be termed the "water of constitution," contained in the molecule of the disodium derivative of diacetylacetone, by acting on diacetylacetone itself with sodium ethoxide suspended in absolutely dry alcohol, since it has been shown (Collie, *Trans.*, 1904, 85, 976) that the compound prepared as previously described, even after being heated under diminished pressure, had the composition C₇H₈O₃Na₂·H₂O.

Some diacetylacetone was carefully dried in a desiccator and then weighed exactly 7.45 grams. The requisite quantity of sodium ethoxide for the reaction was prepared by dissolving 2.5 grams of sodium in 75 c.c. of dry alcohol and the diacetylacetone added. The disodium derivative at once separated; it was filtered, washed with dry alcohol until free from sodium ethoxide, and 20 grams of ethyl iodide (an excess of 3 grams) added. After boiling on the water-bath for two hours in a flask fitted with a reflux condenser, the preparation was left until the following day, when large, colourless plates had separated. Several of these were removed mechanically and rapidly dried between filter-paper and then left for three hours in a desiccator. When dissolved in water, they gave a purple coloration with ferric chloride solution. On analysis, the substance proved to be diethyldiacetylacetone.

0.2025 gave 0.4930 CO₂ and 0.1687 H₂O. C = 66.4; H = 9.2.

C₁₁H₁₈O₃ requires C = 66.6; H = 9.1 per cent.

Diethyldiacetylacetone appears to be a very volatile substance, as the remainder of the crystals left overnight on a porous plate in the air had entirely disappeared by the next day, leaving a slight stain on the white surface of the plate.

Scarcely any dimethylethylpyrone was extracted from the remainder of the contents of the flask, but a very good yield of the diethyl derivative was obtained. This suggests that the presence of water, resulting as it may do in the formation of the monosodium derivative of diacetylacetone, is an important factor in the production of the mono-ethyl compound.

Dimethylpropylpyrone (?) and its Isomeride, C₁₀H₁₄O₂.

Several experiments were made with the object of ascertaining if the action of *n*-propyl iodide on the disodium salt of diacetylacetone would produce compounds similar to those obtained by the action of ethyl iodide. The method of procedure was precisely similar to that employed in the investigation of the action of ethyl iodide. The dried disodium derivative of diacetylacetone was suspended in dry alcohol and a slight excess of the *n*-propyl iodide added. The mixture was then heated on the water-bath until all the solid particles had disappeared and the contents of the flask were of a deep red colour. The alcohol and excess of propyl iodide were distilled off, the latter under slightly reduced pressure, when a considerable amount of sodium iodide separated out. This was removed by filtration and a large excess of strong hydrochloric acid was added and the mixture warmed on the water-bath for two hours. After cooling, the mixture was diluted with water and extracted with chloroform. On distilling off the chloroform, an oil was obtained which boiled at about 205° under 35 mm. pressure.

Only small yields of the oil were obtained as the result of several experiments. It apparently undergoes slight decomposition on distillation under the ordinary atmospheric pressure (b. p. over 300°), since darkening occurs.

After standing for a fortnight, the oil solidified and analysis gave the following result :

0.2004 gave 0.5289 CO₂ and 0.1515 H₂O. C = 71.9 ; H = 8.4.

C₁₀H₁₄O₂ requires C = 72.3 ; H = 8.4 per cent.

The compound gave no coloration with ferric chloride, and at once reduced potassium permanganate solution without warming. It dissolved in acetic acid readily, and bromine water was instantly decolorised. It thus seemed to possess similar properties to those of the corresponding ethyl compound, but sufficient was not obtained for an extended series of experiments.

Dimethylpropylpyrone (?) , C₁₀H₁₄O₂.

The hydrochloric acid solution (left after extraction with chloroform of the oil mentioned above) was heated on the water-bath in a flask and most of the hydrochloric acid removed by distillation under reduced pressure. The solution was then neutralised with sodium carbonate, made faintly acid with dilute hydrochloric acid, and extracted with ether. A very small quantity of a solid substance was left after removal of the ether by evaporation. The total yield from

three successive preparations was less than a gram. It was recrystallised twice from water and dried over sulphuric acid in a desiccator.

0.1998 gave 0.5312 CO_2 and 0.1585 H_2O . $\text{C} = 72.5$; $\text{H} = 8.1$.

$\text{C}_{10}\text{H}_{14}\text{O}_2$ requires $\text{C} = 72.3$; $\text{H} = 8.4$ per cent.

Thus the substance appears to be dimethylpropylpyrone, but it was not characterised by a sharp melting point ($98-101^\circ$). It apparently gives a platinichloride, but too small a quantity was available for analysis.

Repeated attempts to prepare dimethyldipropylpyrone were unsuccessful, only small quantities of the above compound being produced. It would appear that the alkyl iodides of higher molecular weight react with difficulty with disodium diacetylacetone, and experiments are being at present carried out which will finally determine this point.

It is hoped that the evidence as to the constitution of these interesting isomerides may be strengthened later on by means of refractivity experiments and examination of their absorption spectra.

The following is a complete list of the new compounds isolated and analysed :

(1) The compound $\text{C}_9\text{H}_{12}\text{O}_2$ (m. p. $66-67^\circ$, b. p. 289°), isomeric with dimethylethylpyrone.

(2) Dimethylethylpyrone, $\text{C}_9\text{H}_{12}\text{O}_2$ (m. p. 58°).

(3) Dimethylethylpyrone hydrochloride, $(\text{C}_9\text{H}_{12}\text{O}_2)_2, \text{HCl}, 2\text{H}_2\text{O}$.

(4) Dimethylethylpyrone platinichloride, $(\text{C}_9\text{H}_{12}\text{O}_2)_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$.

(5) Dimethyldiethylpyrone, $\text{C}_{11}\text{H}_{16}\text{O}_2$ (m. p. 64°).

(6) Dimethyldiethylpyrone platinichloride,
 $(\text{C}_{11}\text{H}_{16}\text{O}_2)_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$.

(7) Diethyldiacetylacetone, $\text{C}_{11}\text{H}_{18}\text{O}_3$.

(8) Dimethylpropylpyrone, $\text{C}_{10}\text{H}_{14}\text{O}_2$.

(9) The compound $\text{C}_{10}\text{H}_{14}\text{O}_2$ (b. p. 205° under 35 mm. pressure), isomeric with dimethylpropylpyrone.

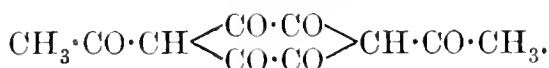
In conclusion, the author of this paper desires to express his sincere thanks to Professor Collie, who suggested this research, and to whom he is deeply indebted not only for constant advice and encouragement during its progress, but also for part of the dehydracetic acid used in the preparation of the dimethylpyrone employed, which was purchased with a grant from the Chemical Society.

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CXXV.—*The Ethyl Esters of Acetonyloxalic and Acetophenyloxalic Acids and the Action of Ethyl Oxalate on Acetanilide and its Homologues.*

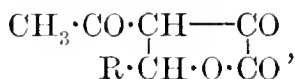
By SIEGFRIED RUHEMANN.

CLAISEN (*Ber.*, 1891, **24**, 128) showed that ethyl sodioacetonyloxalate, when boiled with glacial acetic acid, yielded a violet sodium compound from which other metallic derivatives could be obtained. These he found to have the empirical formula $C_5H_3O_3M'$, but he expressed the view that, most probably, this formula should be doubled, and suggested for the substance from which those salts are derived, the formula :

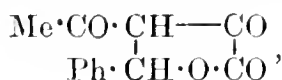


Its formation would accordingly take place by the condensation of two molecules of ethyl acetonyloxalate accompanied by the loss of two molecules of alcohol. Beyond a short notice, no detailed account of this work appeared in the current literature. The fact that the compound which is formed from the product of the reaction between phenylpropionyl chloride and sodioacetylacetone (see Ruhemann and Merriman, *Trans.*, 1905, **87**, 1383 ; Ruhemann, *Trans.*, 1906, **89**, 682) yields blue salts similar to those which are produced from ethyl acetonyloxalate has induced me to subject this ester to a closer study. The investigation of the reaction which leads to the formation of coloured salts from this ester is not yet completed and will form the subject of a later communication. The present paper contains the record of a research on the behaviour of the compounds which are produced by the action of aldehydes on the ethyl esters of acetonyloxalic and acetophenyloxalic acids.

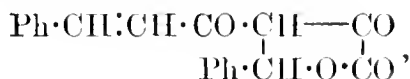
Similar experiments had already been undertaken by Claisen. In a short note (*Ber.*, 1891, **24**, 116) he stated that ethyl acetonyloxalate yielded compounds which might be represented thus :



but a full account of this work did not appear. I have found that, in the presence of piperidine as a catalytic agent, ethyl acetonyloxalate condenses with benzaldehyde to form a substance having the formula

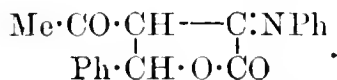


which may be called acetylketophenylparacone. The properties of this substance are analogous to those of ethyl ketophenylparaconate, which W. Wislicenus (*Ber.*, 1892, 25, 3448 ; 1893, 26, 2144) obtained by the action of hydrogen chloride on a mixture of benzaldehyde and ethyl oxaloacetate, and also to those of ketophenylparacophenone, which Knoevenagel (*Annalen*, 1894, 281, 48) prepared in the same way from benzaldehyde and ethyl acetophenyloxalate. On using hydrogen chloride instead of piperidine, two molecules of benzaldehyde react with one molecule of ethyl acetonyloxalate to yield a compound which undoubtedly is to be formulated thus :

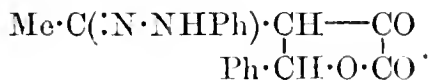


and is therefore benzylideneacetylketophenylparacone. An analogous reaction, however, does not take place on treating a mixture of ethyl acetonyloxalate and *m*- or *p*-nitrobenzaldehyde with hydrogen chloride, but there are formed the corresponding nitro-derivatives of acetylketophenylparacone.

Acetylketophenylparacone, as well as its nitro-derivatives, readily reacts with aniline and its homologues and, with the loss of one molecule of water, yields yellow compounds. The fact that these are insoluble in sodium carbonate fixes their constitution. For example, the substance which is formed from aniline and acetylketophenylparacone must be represented by the formula



With phenylhydrazine, acetylketophenylparacone forms a phenylhydrazone. This differs in its behaviour from the former substances inasmuch as it dissolves in sodium carbonate, especially on warming, and yields a yellow solution from which the hydrazone is precipitated by mineral acids. This property points to the following structure of the compound :



Ketophenylparacophenone, $\begin{array}{c} \text{Ph} \cdot \text{CO} \cdot \text{CH} - \text{CO} \\ | \qquad \qquad | \\ \text{Ph} \cdot \text{CH} \cdot \text{O} \cdot \text{CO} \end{array}$, reacts with aniline and its homologues to form compounds which resemble in every respect those from acetylketophenylparacone.

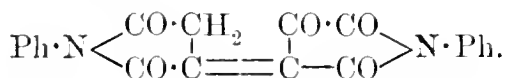
The formation of these yellow substances induced me to examine whether any relation exists between them and the products which W. Wislicenus and Sattler (*Ber.*, 1891, 24, 1245) described as xanthoxalanil and xanthoxalotoluidil. These chemists showed that

the action of sodium ethoxide on a mixture of ethyl oxalate and acetanilide was similar to the formation of ethyl oxaloacetate and yielded ethyl oxaloacetanilide, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$. The amount, however, which was formed was very small, the greater portion of the mixture being transformed into the yellow sodium compound, $\text{C}_{10}\text{H}_6\text{O}_3\text{NNa}$. With regard to the constitution of this substance they

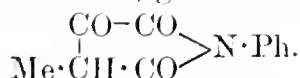
suggested the formula $\begin{array}{c} \text{CO} \text{---} \text{CO} \\ | \\ \text{CHNa}\cdot\text{CO} \end{array} > \text{N}\cdot\text{Ph}$. They found, further, that

oxaloacetanil, $\text{C}_{10}\text{H}_7\text{O}_3\text{N}$, could not be isolated from its metallic derivative because it rapidly changed into a yellow, complicated product. This they proved to be a mixture of anilinomaleic acid, $\text{Ph}\cdot\text{NH}\cdot\begin{array}{c} \text{C} \text{---} \text{CO} \\ || \\ \text{CH} \text{---} \text{CO} \end{array} > \text{N}\cdot\text{Ph}$, and a yellow substance which they were

unable to purify, and since different specimens gave, on analysis, varying results, they did not express a view concerning the composition or the constitution of xanthoxalanil. On using aceto-*p*-toluidide, instead of acetanilide, Wislicenus and Sattler prepared a similar product which they called xanthoxalo-*p*-toluidil. I have been able to obtain these substances as well as xanthoxalo-*o*-toluidil and xanthoxalo- α -naphthylanil in a pure state and to fix their constitution. This differs widely from the structure of the yellow compounds which are formed by the action of aromatic bases on acetyl ketophenylparacone and ketophenylparacophenone. Xanthoxalanil and xanthoxalo-*p*-toluidil, which can be crystallised from hot nitrobenzene, form orange plates, the shade of the latter being the paler; xanthoxalo-*o*-toluidil crystallises from the same solvent in canary-yellow plates, whilst xanthoxalo- α -naphthylanil dissolves in boiling glacial acetic acid and, on cooling, separates in similar crystals. The analytical results lead to the formula $\text{C}_{20}\text{H}_{12}\text{O}_5\text{N}_2$ for xanthoxalanil; its structure must be represented by the formula

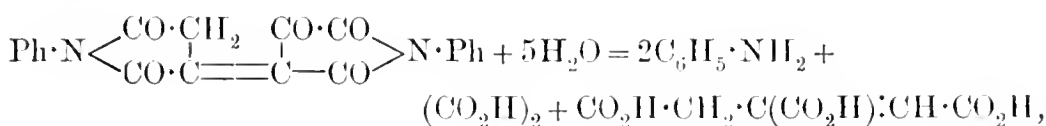


Analogous formulæ must be assigned to the other condensation products. These formulæ are derived from the following considerations. Wislicenus and Sattler (*loc. cit.*) showed that similar substances were not formed if, instead of acetanilide or acetotoluidide, ethyl acetanilide or propionanilide were treated with ethyl oxalate. Ethyl acetanilide thus yielded ethoxalethylacetanilide, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}(\text{Et})\text{Ph}$; propionanilide, on the other hand, gave methyloxalacetanil,



These facts lead to the conclusion that yellow condensation products are produced only from oxalacetanil or those of its derivatives which

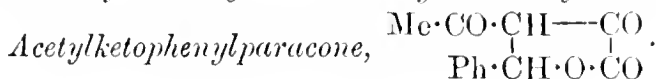
contain the group CH_2 of oxalacetic acid. Oxaloacetanil and oxaloacetotoluidide are stable in the form of their sodium compounds; on acidifying the aqueous solutions of these salts, two of their molecules condense and, with the loss of one molecule of water, yield coloured substances. The circumstance that they dissolve in sodium carbonate is in harmony with the view which I have advanced concerning their structure. The formation of these compounds, therefore, is analogous to the production of indogenides from indoxyl. Wislicenus and Sattler (*loc. cit.*) showed that xanthoxalanil was decomposed on boiling with an alkali, and they isolated as products of the reaction aniline and oxalic acid. It may be expected that this decomposition will take place thus:



and furnish aconitic acid or its stereoisomeride. Experiments are in progress with the view of verifying this assumption.

EXPERIMENTAL.

Action of Aldehydes on Ethyl Acetonyloxalate.

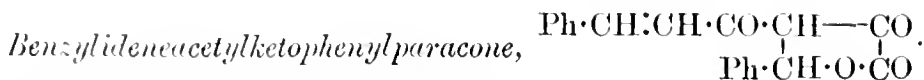


A mixture of ethyl acetonyloxalate (8 grams), benzaldehyde (5.4 grams), and piperidine (about 8 drops), on standing for a few days, deposits crystals, and after a week the whole has set to a semi-solid. The product is filtered with the aid of the pump and crystallised from boiling water, when colourless needles are obtained which melt at $170-171^\circ$.

0.2021 gave 0.4892 CO_2 and 0.0848 H_2O . $\text{C} = 66.01$; $\text{H} = 4.66$.

$\text{C}_{12}\text{H}_{10}\text{O}_4$ requires $\text{C} = 66.05$; $\text{H} = 4.58$ per cent.

The substance distils in a vacuum with but slight decomposition; it is rather soluble in alcohol, but sparingly soluble in boiling water. It has acidic properties and dissolves easily in sodium carbonate or ammonia. On mixing concentrated aqueous solutions of the compound and silver nitrate, a white *silver* salt is precipitated which readily dissolves in water; the solution, on boiling, decomposes and deposits a silver mirror. Acetylketophenylparacone dissolves in cold concentrated sulphuric acid, and is precipitated unchanged on adding water to the yellow solution. With ferric chloride, its solutions yield a deep red coloration.



As stated before (p. 1237), this substance is formed by saturating a well-cooled mixture of benzaldehyde and ethyl acetonyloxalate with dry hydrogen chloride, the result being the same whether aldehyde and ester are used in equimolecular quantities or in the proportion of two molecules of the aldehyde to one mol. of the ester. The brown liquor which is produced on standing overnight sets to a coloured solid. This is washed with cold alcohol and crystallised from the boiling solvent, in which it dissolves with difficulty. It gradually separates in yellow prisms which melt and decompose at 220° . The compound, after drying in a vacuum-desiccator over sulphuric acid, contains one mol. of alcohol which it loses at 100° , the colour changing at the same time to pale yellow.

0.1854, dried at 100° , gave 0.5053 CO_2 and 0.0787 H_2O . $\text{C} = 74.33$; $\text{H} = 4.71$.

0.1873, dried at 100° , gave 0.5124 CO_2 and 0.0798 H_2O . $\text{C} = 74.61$; $\text{H} = 4.73$.

$\text{C}_{19}\text{H}_{14}\text{O}_4$ requires $\text{C} = 74.51$; $\text{H} = 4.57$ per cent.

0.2011, dried in a vacuum at the ordinary temperature, on heating at 100° lost 0.0261. $\text{C}_2\text{H}_6\text{O} = 12.97$.

$\text{C}_{19}\text{H}_{14}\text{O}_4 \cdot \text{C}_2\text{H}_6\text{O}$ requires $\text{C}_2\text{H}_6\text{O} = 13.06$ per cent.

This substance cannot be distilled; it readily dissolves in sodium carbonate, and is precipitated from the solution by mineral acids. On boiling with caustic potash, it decomposes with formation of benzaldehyde.



This compound is prepared by mixing *m*-nitrobenzaldehyde (4.7 grams), dissolved in a little benzene, with ethyl acetonyloxalate (5 grams) and saturating the ice-cold solution with dry hydrogen chloride. The red solid which separates in the course of a day is dissolved in hot dilute alcohol and the solution decolorised with animal charcoal, when colourless prisms are obtained which melt at 170° .

0.1999 gave 0.4000 CO_2 and 0.0618 H_2O . $\text{C} = 54.57$; $\text{H} = 3.43$.

0.2011 „ 0.4033 CO_2 and 0.0636 H_2O . $\text{C} = 54.69$; $\text{H} = 3.51$.

0.2235 „ 10.6 c.c. moist nitrogen at 22° and 761.5 mm. $\text{N} = 5.38$.

$\text{C}_{12}\text{H}_9\text{O}_6\text{N}$ requires $\text{C} = 54.75$; $\text{H} = 3.42$; $\text{N} = 5.32$ per cent.

This substance is rather soluble in alcohol, but difficultly so in boiling water, and the solutions give a red coloration with ferric chloride.

Acetyl keto-p-nitrophenylparacone.

This is produced in the same way as the former substance. For purification it is dissolved in sodium carbonate, and the filtered solution treated with an excess of dilute hydrochloric acid. The solid which is precipitated dissolves in boiling water and, on cooling, crystallises in groups of needles which melt at 177° to a brown liquid.

0.1989 gave 9.4 c.c. moist nitrogen at 21° and 765 mm. $N = 5.41$.

$C_{12}H_9O_6N$ requires $N = 5.32$ per cent.

Action of Aromatic Bases on Acetyl ketophenylparacone and its Derivatives.

This reaction takes place on adding the base to a hot alcoholic solution of acetyl ketophenylparacone or its derivatives, when, after a short time or in the course of a day, the yellow condensation product separates. The constitution of these substances has been already discussed in the introduction.

Acetyl ketophenylparaconanilide, $C_{18}H_{15}O_3N$.

This compound is sparingly soluble in alcohol, but readily so in boiling glacial acetic acid, and on cooling crystallises in yellow prisms. These darken at about 220° and melt and decompose at 230° .

0.2015 gave 0.5435 CO_2 and 0.0934 H_2O . $C = 73.56$; $H = 5.15$.

0.2519 „ 11 c.c. moist nitrogen at 21° and 757 mm. $N = 4.84$.

$C_{18}H_{15}O_3N$ requires $C = 73.72$; $H = 5.12$; $N = 4.78$ per cent.

The anilide is insoluble in sodium carbonate. On boiling with hydrochloric acid, it dissolves and the yellow colour disappears. The solution, on cooling, deposits colourless crystals, which were identified as acetyl ketophenylparacone by the melting point (170°) and chemical properties. The acid filtrate contains aniline. Acetyl ketophenylparacone is not attacked by hydrochloric acid, readily, however, by caustic potash ; its anilide, therefore, on boiling with the alkali, decomposes and yields benzaldehyde as well as aniline.

Acetyl ketophenylparacone-o-toluidide is rather soluble in boiling alcohol and, on cooling, crystallises in yellow prisms which melt at 174° .

0.2509 gave 10.2 c.c. moist nitrogen at 19° and 765.5 mm. $N = 4.65$.

$C_{19}H_{17}O_3N$ requires $N = 4.56$ per cent.

Acetylketo-m-nitrophenylparaconanilide.

This substance separates as a yellow solid on adding aniline to an alcoholic solution of acetylketo-*m*-nitrophenylparacone. It is sparingly soluble in alcohol or boiling glacial acetic acid, and crystallises from the latter solvent in yellow prisms, which darken at about 225° and melt at 237° with evolution of gas.

0.2084 gave 15.2 c.c. moist nitrogen at 20° and 755 mm. $N = 8.28$.

$C_{18}H_{11}O_5N_2$ requires $N = 8.28$ per cent.

Acetylketo-m-nitrophenyl- α -naphthylamide is prepared in the same way by using α -naphthylamine instead of aniline. It is sparingly soluble in boiling alcohol, and, on cooling, crystallises in yellow needles which melt and decompose at 215°.

0.1932 gave 12.4 c.c. moist nitrogen at 24° and 768 mm. $N = 7.27$.

$C_{22}H_{16}O_5N_2$ requires $N = 7.21$ per cent.

Acetylketophenylparaconephenylhydrazone.

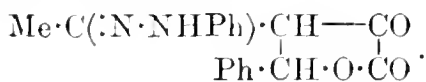
This compound is fairly soluble in hot alcohol, and, on cooling, separates in yellow needles which melt and decompose at 165—166°.

0.2007 gave 0.5160 CO_2 and 0.0953 H_2O . $C = 70.12$; $H = 5.27$.

0.2054 „ 17.4 c.c. moist nitrogen at 25° and 758 mm. $N = 9.41$.

$C_{18}H_{16}O_3N_2$ requires $C = 70.13$; $H = 5.21$; $N = 9.09$ per cent.

The phenylhydrazone is soluble in sodium carbonate, especially on warming. I have already (p. 1237) mentioned that, owing to this fact, its constitution is most probably to be represented thus:



The substance also dissolves in ammonia, and the solution reduces silver nitrate.

Action of Aniline on Benzylideneacetylketophenylparacone.

The product which is formed by the action of hydrogen chloride on a mixture of benzaldehyde and ethyl acetonyloxalate dissolves when heated with alcohol in the presence of aniline. The cold solution does not deposit a solid even after several days; on adding an excess of dilute hydrochloric acid, a yellow substance is precipitated which has been identified as benzylideneacetylketophenylparacone by its proper-

ties and by the following analysis of a specimen which had been recrystallised from alcohol and dried at 100° :

0.2183 gave 0.5940 CO_2 and 0.0910 H_2O . $\text{C} = 74.21$; $\text{H} = 4.63$.

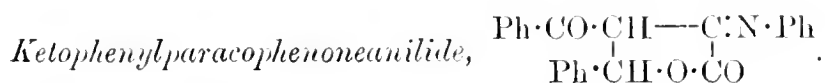
$\text{C}_{19}\text{H}_{14}\text{O}_4$ requires $\text{C} = 74.51$; $\text{H} = 4.57$ per cent.

Condensation of Aromatic Bases with Ketophenylparacophenone.

Ketophenylparacophenone has been obtained by the action of hydrogen chloride on a mixture of benzaldehyde and ethyl acetophenyloxalate. Knoevenagel (*Annalen*, 1894, 281, 48), who prepared this substance in the same way before, stated that it was fairly soluble in boiling alcohol, whilst I find it to dissolve in this solvent with great difficulty. From the solution, on cooling, it crystallises in colourless needles which sinter at 212° and melt at 215° with decomposition. Its formula has been verified by analysis :

0.2036 gave 0.5430 CO_2 and 0.0790 H_2O . $\text{C} = 72.73$; $\text{H} = 4.31$.

$\text{C}_{17}\text{H}_{12}\text{O}_4$ requires $\text{C} = 72.86$; $\text{H} = 4.28$ per cent.



Since ketophenylparacophenoneanilide requires a large quantity of boiling alcohol in order to dissolve it, whilst its condensation product with aniline is rather soluble in this solvent, it is advisable in preparing the latter compound to heat the mixture of alcohol with equal weights of the base and ketophenylparacophenone, when this readily dissolves. The solution, on cooling, deposits yellow, prismatic plates which melt and decompose at $171\text{--}172^{\circ}$.

0.2005 gave 0.5711 CO_2 and 0.0865 H_2O . $\text{C} = 77.67$; $\text{H} = 4.79$.

0.2244 „ 8 c.c. moist nitrogen at 19° and 750 mm. $\text{N} = 4.04$.

$\text{C}_{23}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C} = 77.74$; $\text{H} = 4.78$; $\text{N} = 3.94$ per cent.

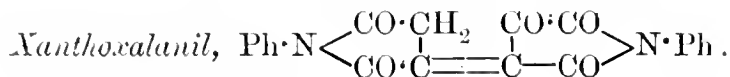
This substance, like the condensation products of acetylketophenylparacone with aniline and its homologues, is insoluble in sodium carbonate.

Ketophenylparacophenone-o-toluidide.

This compound is readily soluble in hot alcohol, and on cooling crystallises in yellow prisms melting at $125\text{--}126^{\circ}$.

0.2300 gave 7.8 c.c. moist nitrogen at 22° and 770 mm. $\text{N} = 3.89$.

$\text{C}_{24}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{N} = 3.79$ per cent.

Action of Acetanilide and its Homologues on Ethyl Oxalate.

This substance was prepared according to the directions of W. Wislicenus and Sattler (*loc. cit.*) by agitating dry sodium ethoxide (1 mol.) with benzene and ethyl oxalate (1 mol.), when, after a short time, the alcoholate dissolves with development of heat. A warm solution of acetanilide (1 mol.) in benzene is then added, and the mixture, after being kept for two days, is shaken with water. On acidifying the aqueous layer, it becomes turbid, and in the course of a few hours deposits a yellow solid, the separation of which is complete after two to three days. The precipitate is collected, washed with alcohol, and, after drying in the water-bath, dissolved in hot nitrobenzene. The dark red solution, on cooling, yields glistening, deep orange plates, which, when recrystallised from the same solvent, melt and decompose at 270—271°.

For analysis, the substance was washed with alcohol to free it from nitrobenzene and dried at 100°.

0.2015 gave 0.4915 CO₂ and 0.0623 H₂O. C = 66.52; H = 3.43.

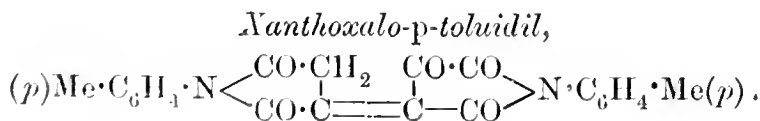
0.2347 „ 15.8 c.c. moist nitrogen at 18° and 765 mm. N = 7.83.

C₂₀H₁₂O₅N₂ requires C = 66.66; H = 3.33; N = 7.78 per cent.

Wislicenus and Sattler stated that they were able to crystallise a small quantity of the product from boiling ethyl oxalate, and that the yellow plates which they thus obtained decomposed above 250°, but they found that the analyses of different specimens did not yield concordant results, the mean being:

C = 66.7; H = 4.2; N = 7.3 per cent.

Xanthoxalanil dissolves, although with difficulty, in cold sodium carbonate and dilute ammonia, and is precipitated from these orange solutions by hydrochloric acid.



Wislicenus and Sattler (*loc. cit.*) showed that ethyl oxalate reacted with aceto-*p*-toluidide under the same conditions as acetanilide, yielding as chief product xanthoxalo-*p*-toluidil, which melted at 259°. On proceeding in the same way as in the previous case and crystallising the

yellow solid which is formed from hot nitrobenzene, orange plates are obtained which have a lighter shade than xanthoxalanil; on heating, they darken at about 255° and melt at 260° with evolution of gas.

0.2018 gave 0.5023 CO_2 and 0.0760 H_2O . $\text{C} = 67.88$; $\text{H} = 4.18$.

0.1988 „ 12.8 c.c. moist nitrogen at 24° and 767 mm. $\text{N} = 7.28$.

$\text{C}_{22}\text{H}_{16}\text{O}_5\text{N}_2$ requires $\text{C} = 68.04$; $\text{H} = 4.12$; $\text{N} = 7.21$ per cent.

Wislicenus and Sattler, who analysed the product after it had been purified as well as possible, found as a mean of their analyses:

$\text{C} = 70.1$; $\text{H} = 4.3$; $\text{N} = 7.0$ per cent.

Xanthoxalo-o-toluidil.

This substance is prepared in the same way as the former compounds by the action of aceto-*o*-toluidide on ethyl oxalate in the presence of sodium ethoxide. It dissolves in hot nitrobenzene more readily than its isomeride, and, on cooling, gradually separates in canary-yellow plates which darken at about 245° and melt at 247° with evolution of gas.

0.2028 gave 0.5043 CO_2 and 0.0803 H_2O . $\text{C} = 67.82$; $\text{H} = 4.39$.

0.2076 „ 13.6 c.c. moist nitrogen at 25° and 762 mm. $\text{N} = 7.32$.

$\text{C}_{22}\text{H}_{16}\text{O}_5\text{N}_2$ requires $\text{C} = 68.04$; $\text{H} = 4.12$; $\text{N} = 7.21$ per cent.

Xanthoxalo- α -naphthylanil,



Aceto- α -naphthalide, which is required for the production of this compound, was prepared by Pinnow's excellent method (*Ber.*, 1900, 33, 418) by dissolving α -naphthylamine in 50 per cent. acetic acid and adding acetic anhydride. The substance is dissolved in dry benzene and mixed with a solution of sodium ethoxide and ethyl oxalate in benzene. The mixture, after being kept for two days, is shaken with water, the aqueous layer filtered from a white solid, and acidified, when, in the course of several hours, a solid is precipitated. This is washed with alcohol and dissolved in boiling glacial acetic acid; on cooling, beautiful yellow plates separate, which decompose at about 285° .

0.2025 gave 10.8 c.c. moist nitrogen at 18° and 765.5 mm. $\text{N} = 6.20$.

$\text{C}_{23}\text{H}_{16}\text{O}_5\text{N}_2$ requires $\text{N} = 6.08$ per cent.

Xanthoxalo- α -naphthylanil, like the other members of this class of

compounds, although almost insoluble in alcohol, dissolves sufficiently to impart to it a yellow colour.

The author is indebted to the Research Fund Committee of the Society for a grant which has partly defrayed the expense of this investigation.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

CXXVI.—*Aldehydrol and the Formation of Hydrates of Compounds containing a Carbonyl Group.*

By WILLIAM MORRIS COLLES, Jun.

THE probable existence of aldehydrol, $\text{CH}_3\cdot\text{CH}(\text{OH})_2$, in aqueous solutions of aldehyde was first pointed out by Ramsay and Young (*Phil. Trans.*, 1886, 1, 117), and confirmed later by Perkin (*Trans.*, 1887, 51, 808) and Brown and Pickering (*Trans.*, 1897, 71, 774). Quite recently, Miss Homfray (*Trans.*, 1905, 87, 1435) has again indicated the existence of this compound. It seemed interesting, therefore, to see if a solid product could be obtained by subjecting concentrated solutions of aldehyde to low temperatures.

The difference between the stability of such compounds as chloral hydrate, dichloroacetaldehyde hydrate, bromal hydrate, and aldehydrol is evidently due to some particular function of the strong electro-negative group contained in the former compounds. The spontaneous elimination of water from aldehydrol may possibly be due to some very rapid internal oscillations in the molecule, which may be sufficiently retarded at low temperatures to render the compound isolable.

The research was subsequently extended to the behaviour of concentrated aqueous solutions of formic acid, acetone, acetic, monochloroacetic and trichloroacetic acids at low temperatures.

Acetone apparently combines only to slight degree in aqueous solution, as shown by Drude (*Zeit. physikal. Chem.*, 1897, 23, 313) and Miss Homfray (*loc. cit.*), nor are any indications to be drawn from the form of the specific gravity curve.

Hexachloroacetone crystallises with one molecule of water (Cloezy, *Ann. Chim. Phys.*, 1886, [vi], 9, 203), possibly forming the compound $\text{CCl}_3\cdot\text{C}(\text{OH})_2\cdot\text{CCl}_3$; the other chloro- and bromo-acetones appear, how-

ever, to form higher hydrates (Clocz, *loc. cit.*; Bischoff, *Ber.*, 1875, 8, 1341; Hantzsch, *Ber.*, 1888, 21, 2441).

Hantzsch (*loc. cit.*) points out that the tribromodinitropropionic acid of Benedikt (*Annalen*, 1877, 184, 255) might quite conceivably be a hydrate of tribromodinitroacetone, $\text{CBr}_3 \cdot \text{C}(\text{OH})_2 \cdot \text{CH}(\text{NO}_2)_2$, there being very little difference between the percentage compositions of the two compounds.

Varenne and Godefroy, working with the chrono-stiloscope (*Compt. rend.*, 1904, 138, 990), found no indications of a monohydrate of acetone, but announced the existence of hydrates containing three and four molecules of water.

There is apparently no physical evidence in favour of the existence of ortho-formic acid. Neither Perkin (*Trans.*, 1886, 49, 781) nor Miss Homfray (*loc. cit.*) obtained any values indicating combination between the acid and water. Lorin (*Zeit. Chem.*, 1865, [ii], 1, 692) mentions the hydrate $3\text{CH}_2\text{O}_2, 2\text{H}_2\text{O}$, and Roscoe (*Annalen*, 1863, 125, 329) showed that the hydrate $4\text{CH}_2\text{O}_2, 3\text{H}_2\text{O}$ formed a constantly boiling mixture.

The only evidence in favour of the existence of ortho-acetic acid is the form of the specific gravity curve of the aqueous solution, which shows a maximum density with an equimolecular mixture. Perkin (*loc. cit.*) found, however, no traces of combination, nor did Pickering (*Trans.*, 1895, 67, 669) find any definite hydrates. Sonstadt (*Jahresber.*, 1878, 34) mentions that the anhydrous acid crystallises out on cooling to 0° a solution containing 71 per cent.

Perkin found no indications of any combination in the aqueous solutions of monochloro- and trichloro-acetic acids (*Trans.*, 1894, 65, 406).

It seemed probable, however, that at low temperatures the product of combination of the tricarbinol group $-\text{C}(\text{OH})_3$, with a strong electro-negative group, might become sufficiently stable to be isolated.

The hydrates obtained, however, like those of acetic acid, were exceedingly viscid and consequently very difficult to wash; hence the results, which in the cases of acetic acid and monochloroacetic acid point to the formation of an ortho-acid, are very inconclusive.

EXPERIMENTAL.

A weighed quantity of the substance under investigation was mixed with water in definite molecular proportions, the requisite amount of water being added from a burette reading to 0.01 c.c. The mixture was contained in a long, stoppered weighing tube, which was clamped inside a wide vacuum vessel containing the freezing mixture.

The filtering and stirring apparatus consisted of a piece of quill tubing terminating in a small glass rose packed with glass wool. Two small wings of flattened glass rod were sealed on just above the rose.

The other end of the tube passed through a brass pulley rotated by a water turbine.

The apparatus was clamped so as to rotate as close to the bottom of the weighing tube as possible, and in order that the hydrate mixture should be thoroughly stirred not more than 3—4 c.c. were taken at a time, the glass wings being just covered. A ring-shaped stirrer was used to ensure constant cooling throughout the freezing mixture, the temperature being indicated by an alcohol thermometer.

The freezing mixture first used consisted of a mixture similar to that in the inner tube, but made with commercial preparations. This was cooled by pouring in liquid air, and, being impure, consequently crystallised out a few degrees lower than the hydrate mixture, thus preventing too steep a gradient of temperature between the two. In the case of a mixture of aldehyde and water in molecular proportions, sudden and complete solidification took place at about -60° , a hard, opaque, snow-like mass being formed. This prevented any observation of the inner tube, and frequently twisting it out of centre caused breakage.

Absolute alcohol cooled by pouring in liquid air was found to work very satisfactorily.

The rate of lowering the temperature can be very easily controlled, and down to -100° the alcohol, although becoming slightly viscous, remains perfectly transparent and easy to stir. To prevent too steep a gradient of temperature between the hydrate mixture in the inner tube and the freezing mixture, the rate of lowering must be very gradual, especially when approaching the deposition point of a hydrate, a few minutes being allowed to elapse between each addition of liquid air.

The hydrate mixture must be very thoroughly and rapidly stirred, especially at low temperatures, to prevent ice forming on the walls of the tube. As soon as crystals begin to form, cooling and stirring are stopped and the mother liquor filtered off at once, connection being made with the top of the stirring-tube by means of pressure tubing. The mother liquor was collected in a small vessel in circuit with the water-pump in case an analysis of it should be necessary.

The crystals were dried as completely as possible by unclamping the inner tube and pressing the mass of crystals against the glass rose. In the case of the hydrates of acetic acid and the chloroacetic acids, the crystals were exceedingly viscous and difficult to dry thoroughly.

The great fault of the apparatus lies in the difficulty of washing the crystals thoroughly, but in cases where a good yield was obtained the crystals were allowed to melt partially and were again filtered, thus being washed in a liquid of their own composition. The temperatures given in the results are those of the freezing mixture at the moment of deposition of the hydrate, and were checked by a number of observations.

The thermometer was not standardised against a pentane thermometer, but the error is probably no greater than the actual difference of temperature between the two mixtures.

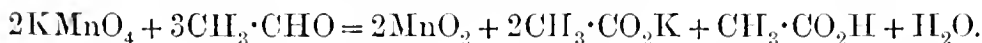
Considerable difficulty was at first experienced in handling aqueous solutions of aldehyde, owing to the very rapid change of concentration due to the volatility of the substance. The following was found to be a quick and easy method for weighing out such solutions.

A three-inch by half-inch test-tube is constricted in the middle to about five mm. diameter and tared. The lower half is then placed in a hole cut in a small block of ice and the solution poured in, the air escaping through a small capillary introduced into the tube. The operation is performed as quickly as possible, and the tube sealed off at the constriction. When cool, the lower half containing the aldehyde is removed from the ice-block and weighed together with the upper half.

This method was found to be very useful when dealing with small quantities of solutions, and especially those containing a very volatile constituent. In the latter case, the ordinary method of filling into bulbs is much too slow, the rate of change of concentration being very rapid in the case of aldehyde and water, for example.

Aldehyde.

Estimation.—The aldehyde was estimated by oxidising with a known excess of potassium permanganate, determining the excess remaining after the reaction. The action was found to proceed best in neutral solution, three of the available atoms of oxygen being used and hydrated manganese dioxide being precipitated:



The excess of permanganate and manganese dioxide was estimated by adding sulphuric acid and a known excess of ferrous ammonium sulphate, titrating back with decinormal permanganate. Later, the quicker method (titrating the iodine liberated from potassium iodide by potassium permanganate in the presence of sulphuric acid with decinormal sodium thiosulphate) was used.

The whole operation was carried out in large, strong, accurately-stoppered bottles, in which the tube of aldehyde was broken into the excess of permanganate. The method is very quick, and a large number of analyses can be carried out at the same time, but it is not very accurate. The error is ± 0.3 per cent., the iodine method giving the higher results.

The aldehyde used was obtained from Marquart, and was stored in small quantities in sealed-up glass bulbs.

Weight of aldehyde taken.	Weight of aldehyde found.	Weight of aldehyde taken.	Weight of aldehyde found.
0.6551 gram	0.6575 gram	0.6955 gram	0.6945 gram
0.4228 "	0.4220 "	0.2409 "	0.2420 "
0.5838 "	0.5821 "	0.2683 "	0.2671 "

It was found in all these experiments that the composition of the crystals deposited usually varies considerably from that of the mixture taken.

Mixture taken in molecules.		Percentage of aldehyde found in crystals.	Nearest corresponding hydrate, with percentage of aldehyde.	Deposition temperature.
Aldehyde.	Water.			
1	1	$\left\{ \begin{array}{l} 51.6 \\ 51.7 \end{array} \right\}$	$C_2H_4O, 2H_2O = 55$ per cent.	-55°
1	3	61.4	$2C_2H_4O, 3H_2O = 62$ "	-80
2	1	$\left\{ \begin{array}{l} 72.6 \\ 69.31 \\ 70.01 \\ 69.82 \end{array} \right\}$	$C_2H_4O, H_2O = 71$ "	-90

These results are from analyses of crystals separated at the moment of formation. By sudden and prolonged cooling and stirring to -95° a mixture containing $2C_2H_4O, H_2O$ yielded crystals containing 78.6 per cent. of aldehyde, that is, the mixture almost solidifies as a whole.

Although the mixture is cooled to as low as 90° , it remains perfectly clear until the last moment, crystallisation taking place very suddenly.

The crystals present the appearance of very fine needles, and are obtained in fair yield.

Formic Acid.

The acid was estimated by titration with decinormal ammonia, giving very sharp end-points.

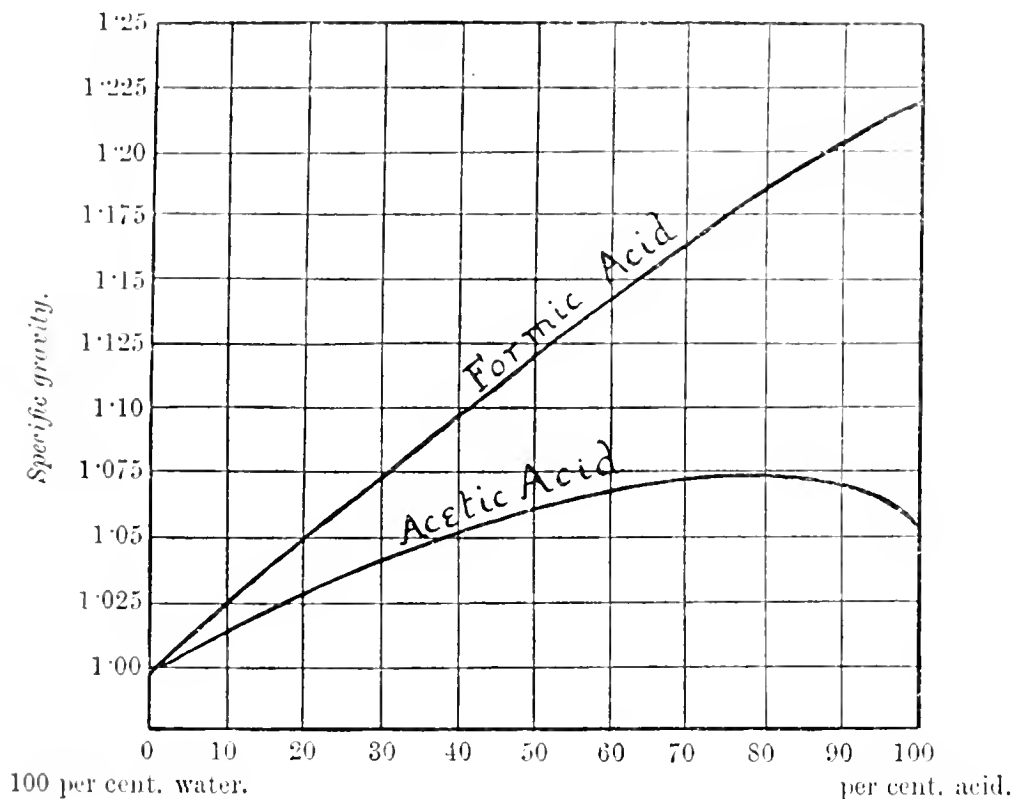
Mixture taken in molecules.		Percentage of formic acid found in crystals.	Nearest corresponding hydrate and percentage of formic acid.	Deposition temperature.
Formic acid.	Water.			
1	1	$\left\{ \begin{array}{l} 59.5 \\ 59.9 \\ 59.4 \\ 60.5 \\ 58.9 \end{array} \right\}$	$4CH_2O_2, 7H_2O = 61.4$ per cent.	-46°
1	2	$\left\{ \begin{array}{l} 39.2 \\ 39.2 \\ 37.9 \end{array} \right\}$	$CH_2O_2, 4H_2O = 38.9$ "	$-36-37$
1	4	$\left\{ \begin{array}{l} 22.08 \\ 25.03 \end{array} \right\}$	$CH_2O_2, 9H_2O$ approximately	$-20-25$
2	1	$\left\{ \begin{array}{l} 77.5 \\ 76.8 \end{array} \right\}$	$4CH_2O_2, 3H_2O = 77.4$ per cent.	-44.5
4	3	$\left\{ \begin{array}{l} 70.25 \\ 69.1 \\ 70.09 \\ 73.75 \end{array} \right\}$	$CH_2O_2, H_2O = 71.8$ "	-53.7
3	1	$\left\{ \begin{array}{l} 78.5 \\ 79.3 \end{array} \right\}$	$3CH_2O_2, 2H_2O = 79.4$ "	-28

As in the case of aldehyde and water, a mixture of formic acid and water is ultimately reached which, on prolonged cooling and stirring, deposits crystals of almost identical composition.

Thus, a mixture having the composition $4\text{CH}_2\text{O}_2, 3\text{H}_2\text{O}$ with rapid cooling deposits crystals containing 76.7 and 77.2 per cent. of formic acid. The hydrate formed in this way at -54° is, however, produced at higher temperatures from a mixture of the composition $2\text{CH}_2\text{O}_2, \text{H}_2\text{O}$.

By very slow and careful cooling and rapid stirring, the mixture of

FIG. 1.



composition $4\text{CH}_2\text{O}_2, 3\text{H}_2\text{O}$ deposits a monohydrate, which, however, must be filtered as soon as crystallisation begins.

The hydrates are distinctly crystalline and can be washed, the temperature of deposition for the monohydrate, -53.7° , being maintained very constantly.

Acetone.

Estimation.—The acetone was estimated by the method of Squibb, described in Sutton's *Volumetric Analysis*.

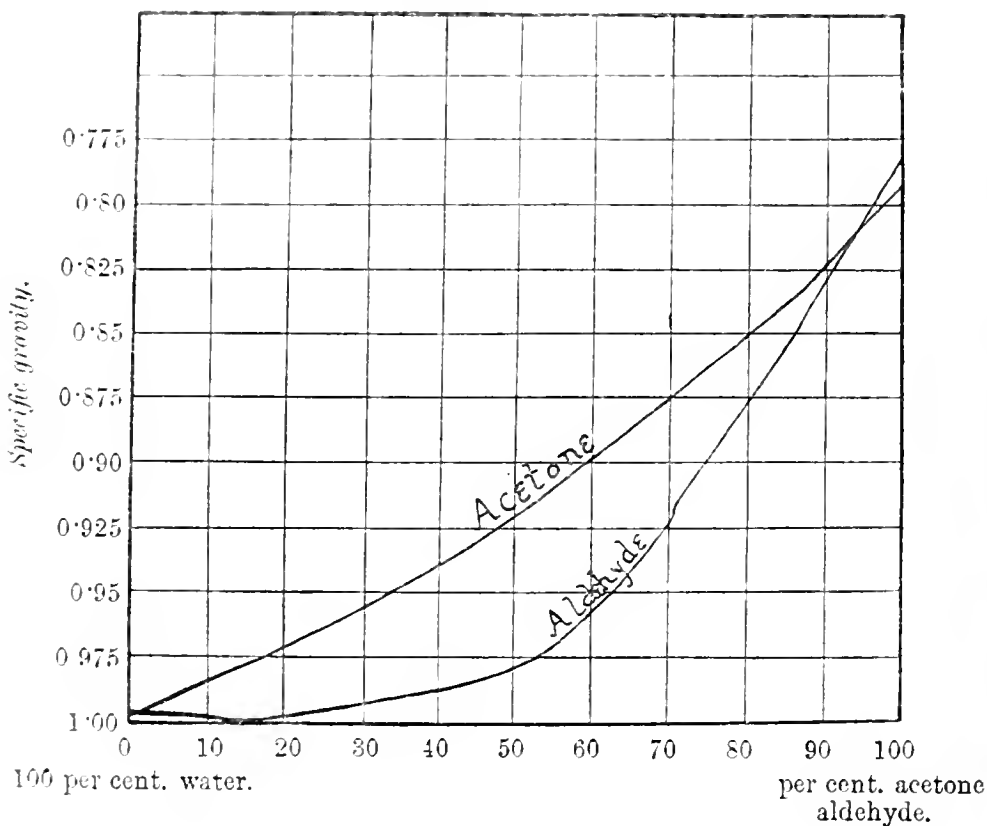
Per cent. of acetone in an aqueous solution : (i) 68.83 ; mean of three titrations.
 " " " " " (ii) 69.20 ; mean of three titrations.

No trace of any monohydrate was found. Many experiments were carried out, but in no case did the percentage of acetone in the crystals rise above 30, and this value, curiously enough, was obtained by cooling an equimolecular solution to -44° , stronger mixtures yielding crystals containing 10—15 per cent. of acetone precipitated at -49° .

The crystals were very minute and only very small yields were obtained, stronger cooling having no effect on the composition or yield.

After drying, the product was left as a fine white powder. Varenne

FIG. 2.



and Godefroy (*loc. cit.*) also obtained hydrates with 8 and 34 molecules of water.

Acetic Acid. Monochloroacetic Acid. Trichloroacetic Acid.

These acids were estimated by titrating with decinormal barium hydroxide, using phenolphthalein as an indicator. Kahlbaum's preparations were used.

The experiments on these acids met with little success. The crystals formed were very small and viscous, repeatedly stopping up the filtering tube. Washing and drying were therefore matters of great

difficulty. The stirring in these experiments had to be exceedingly rapid.

Mixture taken in molecules.		Percentage of acetic acid found in crystals.	Nearest corresponding hydrate and percentage of acetic acid.	Temperature of deposition.
Acetic acid.	Water.			
1	1	$\left\{ \begin{array}{l} 66.4 \\ 66.6 \end{array} \right\}$	$C_2H_4O_2, 2H_2O = 62$ per cent.	-33.5°
2	1	$\left\{ \begin{array}{l} 79.01 \\ 78.6 \end{array} \right\}$	$C_2H_4O_2, H_2O$ $CH_3 \cdot C(OH)_3 = 77$..	-15
1	2	$\left\{ \begin{array}{l} 50.3 \\ 49.4 \\ 55.6 \end{array} \right\}$	$C_2H_4O_2, 3H_2O = 52.6$..	-11

Monochloroacetic Acid.

In the case of this acid, as with trichloroacetic acid, it was found difficult to prevent the anhydrous acid crystallising from the solutions. The stirring was consequently begun with the slightly warm solutions.

Mixture taken in molecules.		Percentage of acid found in crystals.	Nearest hydrate and percentage of acid.	Temperature of deposition.
$CH_2Cl \cdot CO_2H$.	Water.			
1	1	$\left\{ \begin{array}{l} 82.2 \\ 80.55 \end{array} \right\}$	$CH_2Cl \cdot CO_2H, H_2O$ $CH_2Cl \cdot C(OH)_3 = 84$ per cent.	0°

Trichloro-
acetic acid,
 $CCl_3 \cdot CO_2H$.

1	1	$\left\{ \begin{array}{l} 77.55 \\ 77.00 \\ 79.25 \end{array} \right\}$	$CCl_3 \cdot CO_2H, 3H_2O = 75$ per cent. $CCl_3 \cdot CO_2H, 2H_2O = 82$..	-35
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It was found impossible to work with stronger solutions of trichloroacetic acid, as they had to be boiled in order to dissolve the whole of the acid.

The hydrates of these acids, although crystalline, do not precipitate so sharply as those of formic acid. Further experiments were tried, but no better values were obtained, the viscous precipitates being always very difficult to wash.

In conclusion, I wish to express my gratitude to Professor Sir William Ramsay, who suggested this research, for his advice and encouragement; also to Professor J. N. Collie for the kindly interest he has taken in the work.

UNIVERSITY COLLEGE,
LONDON.

CXXVII.—*Studies on Optically Active Carbimides. IV.*
The Resolution of ac-Tetrahydro-2-naphthol by
means of l-Menthylcarbimide.

By ROBERT HOWSON PICKARD and WILLIAM OSWALD LITTLEBURY, A.I.C.

IN Part III (this vol., p. 467) we have described a method of using *l*-menthylcarbimide for the resolution of inactive hydroxyl compounds containing asymmetric carbon atoms. The method was illustrated by the resolution of α -phenyl- α' -4-hydroxyphenylethane, the dextro-isomeride of which was obtained by the hydrolysis of the pure (*dl*) menthylcarbamate after this had been separated by fractional crystallisation from the (*ll*) menthylcarbamate.

The method is, of course, closely allied in principle to Pasteur's method of resolving an inactive acid by the fractional crystallisation of the mixture of stereoisomeric salts obtained by combining the acid with an active base. This resolution was apparently the first successful attempt to resolve a hydroxy-compound by the fractional crystallisation of its two stereoisomeric esters with an optically active acid, in this case the unstable *l*-menthylcarbamic acid. It might be urged, however, that this compound by reason of its slight acidity, due to the phenolic hydroxy-group, might conceivably have been resolved by means of Pasteur's original method. We therefore thought it of interest to describe the application of the method to the resolution of *ac*-tetrahydro-2-naphthol, a compound possessing true alcoholic properties.

The method of procedure is very similar to that described in Part III (*loc. cit.*). The *l*-menthylcarbimide combines readily with the inactive *ac*-tetrahydro-2-naphthol, and yields a mixture of (*dl*) and (*ll*) carbamates, of which the (*dl*) isomeride is less soluble in dilute alcohol than the (*ll*). The subsequent hydrolysis of the carbamate by alcoholic sodium hydroxide presented no difficulty, as *d-ac*-tetrahydro-2-naphthol is not racemised by prolonged boiling with alcoholic alkaline solutions. As a general rule, the racemisation of optically active alcohols does not seem to be induced by mild treatment with alkalis. This is notably the case with borneol, menthol, &c., whilst P. F. Frankland and Price (Trans., 1897, 71, 256) found that amyl alcohol was only readily racemised by sodium and hardly affected by the hydroxide.

It is interesting to compare the properties of the optically active 1:2:3:4-tetrahydro-2-naphthol with those of the optically active

1:2:3:4-tetrahydro-2-naphthylamine (Pope and Harvey, *Trans.*, 1901, 79, 83) and 1:2:3:4-tetrahydro-2-naphthoic acid (Pickard and Yates, this vol., p. 1101).

The ease with which the free base is racemised (doubtless owing to the configuration of the nitrogen atom) is in marked contrast to the stability of the alcohol and the acid, which are not racemised by mild treatment with alkalis.

Whilst a strict comparison of rotatory power of such dissimilar compounds is impossible, the following table shows that the molecular rotatory power of the amine, acid, and alcohol are approximately as 3:2:1.

Molecular Rotatory Power.

	Amine.	Acid.	Alcohol.
Alone at 16°	137°*	—	—
In CHCl ₃	—	91.2°	41.7°
In C ₆ H ₆	—	87.9°	40.9°
Active ion in water.....	130°	90.5°	—

EXPERIMENTAL.

The *ac*-tetrahydro-2-naphthol was prepared by the method of Bamberger and Lodter (*Ber.*, 1890, 23, 205) by the reduction of 2-naphthol by sodium in amyl alcoholic solution, and boiled at 145—148° under a pressure of 20 mm.

d-ac-Tetrahydro-2-naphthyl l-Menthylcarbamate.

The inactive alcohol (1 mol.) was heated in a sealed tube with *l*-menthylcarbimide (1 mol.) at 100° for forty hours. After cooling, the mixture set to a waxy mass and was then repeatedly crystallised from dilute alcohol (about 70—80 per cent.). The first crop melted very indefinitely at 104—109° and had $[\alpha]_D -45.7^\circ$ in chloroform and $[M]_D -150.4^\circ$. The latter value approximates to the fairly constant value of the molecular rotatory power of the various esters of *l*-menthylcarbamic acid described in Part II (this vol., p. 93).

The pure (*dl*) carbamate, obtained after about seven crystallisations, melts sharply at 131° and has $[\alpha]_D -33.4^\circ$ in chloroform and $[M]_D -110^\circ$.

The following table shows the course of one of the separations:

* Calculated from the figures given in the paper by Pope and Harvey (*loc. cit.*).

	Melting point.	$[\alpha]_D$ in CHCl_3 .
1st crop.....	104—109°	- 45·7°
2nd „	106—116	- 43·5
3rd „	106—116	- 42·3
4th „	105—119	- 40·8
5th „	126	- 37·6
6th „	130	- 34·3
7th „	131	- 33·3
8th „	131	- 33·3

The (*d*l) carbamate crystallises in silky needles, is insoluble in water, but dissolves easily in the common organic media except cold light petroleum and alcohol. It is not volatile with steam.

0·2945 gave 12·0 c.c. nitrogen at 24° and 750 mm. $N = 4·50$.

$\text{C}_{21}\text{H}_{31}\text{O}_2\text{N}$ requires $N = 4·25$ per cent.

1·1339 grams made up to 20 c.c. with chloroform gave $\alpha_D - 3·79^\circ$,* whence $[\alpha]_D - 33·4^\circ$ and $[M]_D - 110^\circ$.

d-ac-Tetrahydro-2-naphthol.

4·6 grams of the (*d*l) carbamate were heated in a reflux apparatus with 50 c.c. of alcoholic sodium hydroxide (3*N*/4) for twenty-four hours. The alcohol was then evaporated and the residue, after neutralisation with dilute hydrochloric acid, distilled with steam. The hydrolysis was practically complete, only 0·1 gram of unchanged carbamate remaining in the flask. The distillate was extracted with ether and yielded 2·2 grams of a pale yellow oil which, after desiccation had $[\alpha]_D + 25·6^\circ$ in chloroform. It was distilled under reduced pressure, yielding 1·9 grams of a pale yellow refractive oil boiling at 155—160° (25 mm.).

1·9238 grams made up to 25 c.c. with chloroform gave $\alpha_D + 4·34^\circ$, whence $[\alpha]_D + 28·20^\circ$ and $[M]_D + 41·7^\circ$.

1·8804 grams made up to 25 c.c. with benzene gave $\alpha_D + 4·16^\circ$, whence $[\alpha]_D + 27·65^\circ$ and $[M]_D + 40·9^\circ$.

0·8 gram was heated with *l*-menthylcarbimide (equal mols.) for twenty-four hours in a sealed tube at 100°. The product was hard, brittle, and partly crystalline. After one crystallisation from alcohol it was obtained in silky needles melting at 131°. A polarimetric observation showed that no racemisation took place during the hydrolysis of the carbamate.

0·5958 gram made up to 20 c.c. with chloroform gave $\alpha_D - 1·98^\circ$, whence $[\alpha]_D - 33·23^\circ$.

* The polarimetric observations recorded in this paper were made in a 2-dem. tube.

d-ac-Tetrahydro-2-naphthyl Phenylcarbamate.

The phenylcarbamate was prepared in order to characterise the active alcohol. Equivalent quantities of the active alcohol and phenylcarbimide were mixed and allowed to stand for sixteen hours, when the mixture set to a crystalline mass. This was pressed on a porous plate and extracted with dry ether. The extract crystallised from dilute alcohol in microcrystalline needles which melted at 115—117° [Bamberger and Lodter (*loc. cit.*) give the melting point of the phenylurethane of the inactive alcohol as 98·5°].

0·2760 gave 13·1 c.c. of nitrogen at 20° and 748 mm. $N = 5·34$.

$C_{17}H_{17}O_2N$ requires $N = 5·24$ per cent.

1·0112 grams made up to 20 c.c. with chloroform gave $\alpha_D + 2·55^\circ$, whence $[\alpha]_D + 25·21^\circ$ and $[M]_D + 67·3^\circ$.

0·9192 gram made up to 19·9 c.c. with benzene gave $\alpha_D + 2·97^\circ$, whence $[\alpha]_D + 32·14^\circ$ and $[M]_D + 85·8^\circ$.

l-ac-Tetrahydro-2-naphthol.

The mother liquor from the first crystallisation of the crude carbamate on evaporation deposited a further crop of crystals. These were filtered and the solution evaporated further, when an oil separated which would not crystallise. This was extracted with ether and the extract distilled with steam. The portion not volatile with steam was again extracted with ether and yielded an impure (*ll*) carbamate, which melted indefinitely at about 102° and had $[\alpha]_D - 54·02^\circ$ in chloroform. This product was hydrolysed with alcoholic sodium hydroxide as before and yielded a pale yellow oil which gave the following result in the polarimeter.

1·2421 grams made up to 20 c.c. with chloroform gave $\alpha_D - 2·24^\circ$, whence $[\alpha]_D - 18·03^\circ$. The product then contained about 80 per cent. of the *levo*-alcohol.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant defraying much of the cost of this work.

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CXXVIII.—*The Constitution of Acetone.*

By MILLICENT TAYLOR.

SOME fifteen years ago a series of papers was published by Freer (*Amer. Chem. J.*, 1890, 12, 356; 1891, 13, 322; 1893, 15, 582; *Annalen*, 1893, 278, 116; 1894, 283, 380), showing that sodium directly displaces hydrogen in acetone, and that the resulting "sodium acetone" yields isopropenyl esters with acid chlorides.

Repeated want of success in attempting to prepare isopropenyl esters from sodium acetone led to the further investigation of the action of sodium on acetone, and the behaviour of the resulting substances with acid chlorides.

The determination of the percentage of sodium in so-called "sodium acetone" shows that this substance consists chiefly of caustic soda mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone.

The action of "sodium acetone" on ethyl chloro-formate yielded sodium carbonate together with small quantities of ethyl isopropyl carbonate and large quantities of condensation products of acetone. No indication of the formation of ethyl isopropenyl carbonate was obtained.

The action of "sodium acetone" on *p*-nitrobenzoyl chloride yielded *p*-nitrobenzoic acid and anhydride, sodium *p*-nitrobenzoate, and a small quantity of isopropyl *p*-nitrobenzoate.

The yield of these substances showed conclusively that, allowing for slight loss in the various processes carried out, the total quantity of *p*-nitrobenzoyl chloride was accounted for, and that consequently isopropenyl *p*-nitrobenzoate could not have been formed.

Finally, the action of Grignard's reagent on acetone itself was investigated, but only negative results were obtained, no methane being liberated.

The rapid action of sodium on an ethereal solution of acetone is probably due primarily to traces either of moisture or of caustic soda. When every precaution is taken to dry the acetone and the ether employed as solvent, sodium does not act immediately, but reaction becomes evident in a few minutes and then proceeds rapidly. Heintz (*Annalen*, 1875, 178, 342) and later Koelichen (*Zeit. physikal. Chem.*, 1900, 33, 129) have shown that acetone condenses at 0° and at the ordinary temperature under the influence of caustic soda, yielding diacetone-alcohol, $\text{OH}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$.

This ketone alcohol is readily acted on by sodium, and further loses

water, especially in the presence of dehydrating agents, giving mesityl oxide.

It follows then that the presence of traces of caustic soda, which are most difficult to avoid, would easily account for its further formation in quantity and for the various phenomena observed.

I. *The Determination of the Percentage of Sodium in "Sodium Acetone."*

The ether used in this experiment was dried over phosphorus pentoxide, then left for a week in the dark over repeatedly renewed sodium and potassium wire, and finally boiled for some hours with these metals. The acetone was shaken repeatedly with phosphorus pentoxide and distilled through a Young's still-head. It boiled constantly at 56.2° under 760 mm. The hydrogen was purified by means of caustic soda, soda-lime, calcium chloride, sulphuric acid, and phosphorus pentoxide.

The apparatus was arranged exactly as described by Freer (*Amer. Chem. J.*, 1893, 15, 587), except that a slight modification was introduced in order to bring about more rapid filtration.

The sodium dissolved with the formation of a white precipitate which settled rapidly, and this was followed by the gradual separation of a less dense red substance. After standing for one hour, the precipitate was washed by decantation with absolute ether, and finally some of it was drawn into a funnel tube, washed, and dried in a current of hydrogen until there was no further decrease in weight. The solid was then dissolved in water and titrated with normal sulphuric acid.

0.6275 required 10.25 c.c. *N*-sulphuric acid. Na = 37.5.

"Sodium acetone" requires Na = 28.75 per cent.

A second determination of the sodium in the precipitate, which had been left for twenty-four hours in an atmosphere of hydrogen, showed that the percentage of sodium had decreased.

0.7968 required 11.5 c.c. *N*-sulphuric acid. Na = 33.

The latter result is approximately the percentage of sodium required by "sodium acetone," but since there was no doubt that the formation of the red substance was due to some secondary change, and not to the direct action of sodium on acetone, the solid was not allowed to settle in the next experiments, but the liquid was filtered as soon as it was certain that the whole of the sodium had dissolved.

In two experiments, therefore, 0.7 gram and 0.5 gram of sodium respectively were dissolved in a larger proportion of acetone than had been used previously; in five minutes, the whole of the sodium had disappeared, and the mixture was then stirred for ten minutes, the

precipitate collected, dried in a current of hydrogen until its weight was constant, then dissolved in water and titrated with standard sulphuric acid.

Expt. II. 0.2619 required 114.8 c.c. $N/20$ H_2SO_4 . $Na = 50.4$.

Expt. III. 0.4806 „ 105.4 c.c. $N/10$ H_2SO_4 . $Na = 50.4$.

$NaOH$ requires $Na = 57.5$ per cent.

The ethereal solution in experiments I and III was evaporated in a current of hydrogen. It contained the red precipitate which formed after decantation or filtration, and also some liquid condensation products of acetone, so that the result is of no value as indicating the composition of the red substance.

Expt. I. 0.69 of residue required 35.6 c.c. $N/10$ H_2SO_4 . $Na = 11.9$.

Expt. III. 1.645 of residue required 82.5 c.c. $N/10$ H_2SO_4 . $Na = 11.5$ per cent.

This result is recorded because it has been stated (*Amer. Chem. J.*, 1893, **15**, 587; *Annalen*, 1893, **278**, 116) that this residue has a composition identical with that of the first precipitate and approximately that of "sodium acetone."

II. *The Action of Ethyl Chloro-formate on "Sodium Acetone."*

The reaction was carried out several times under slightly different conditions and using different quantities of materials, but always in accordance with the directions given by Freer (*Amer. Chem. J.*, 1891, **13**, 319; *Annalen*, 1894, **283**, 380).

In each case the result was the same. Large quantities of difficultly-volatile condensation products of acetone were obtained, together with a mixture consisting almost entirely of mesityl oxide, diethyl, ethyl isopropyl and di-isopropyl carbonates, boiling between 120° and 140° .

Details of three of these preparations are recorded here, as the results not only give no indication of the production of ethyl isopropenyl carbonate, but they afford a totally different and yet satisfactory explanation of the facts which have been interpreted as indicating the formation of that ester.

Preparation I.—The volatile products of the reaction, after treatment with phenylhydrazine (the substance used by Freer to remove condensation products of acetone), gave on analysis a percentage of carbon greatly in excess of that calculated for ethyl isopropenyl carbonate. The substances containing this high percentage of carbon can be removed by phenylhydrazine, but only on prolonged treatment

with this reagent, and they are rapidly decomposed by dilute sulphuric acid, leaving only ethyl isopropyl carbonate.

Condensation products of acetone would, however, contain a higher percentage of carbon than ethyl isopropenyl carbonate, and, moreover, are decomposed by dilute sulphuric acid with formation of acetone; so that although the results of this preparation do not prove the absence of ethyl isopropenyl carbonate, they certainly indicate that such condensation products, which I have shown are difficult to remove, may be the source of the acetone stated (*Annalen*, 1894, 283, 380) to have been obtained by saponification of the esters.

Ten grams of sodium, in separate quantities of one gram, were treated with acetone in ethereal solution, and subsequently with ethyl chloroformate, as described by Freer (*Amer. Chem. J.*, 1891, 13, 319). The ether was evaporated and the residue fractionated under a pressure of 250 mm., when half of the liquid product passed over between 90° and 110°. After treatment with phenylhydrazine, the liquid was distilled with steam, dried, and repeatedly fractionated. The largest fraction boiled between 95° and 96° (250 mm.) and gave the following data on analysis:

0.2102 gave 0.4774 CO₂ and 0.1858 H₂O. C = 61.94; H = 9.82.

Ethyl isopropenyl carbonate, C₆H₁₀O₃, requires C = 55.38; H = 7.69.

Mesityl oxide, C₆H₁₀O, requires C = 73.47; H = 10.20 per cent.

It was found that the liquid boiling between 95° and 96° was capable of reacting still further with phenylhydrazine, although the reaction was extremely slow, and after being allowed to remain in contact with excess of this reagent for four days, it was again purified, and the analyses given below show that a further quantity of some condensation product of acetone had been removed.

0.2886 gave 0.2482 H₂O and 0.6358 CO₂. C = 59.46; H = 9.56 per cent.

Five grams of this liquid were then digested for about fifteen minutes on the water-bath with very dilute sulphuric acid, to decompose condensation products of acetone. As soon as the slow formation of small bubbles of gas indicated the incipient decomposition of carbonic esters, the remaining liquid was washed, dried over calcium chloride, and distilled.

It was then found to boil between 91° and 94° under 200 mm. pressure, and appeared from the analysis to be almost pure ethyl isopropyl carbonate.

(I) 0.2739 gave 0.5497 CO₂ and 0.2246 H₂O. C = 54.78; H = 9.11.

(II) 0.1147 „ 0.2300 CO₂ and 0.0953 H₂O. C = 54.68; H = 9.23.

C₆H₁₂O₃ requires C = 54.54; H = 9.09 per cent.

A comparison of the properties of this substance with synthetic ethyl isopropyl carbonate, formed by the action of ethyl chloro-formate on sodium isopropoxide, showed that the two were identical in every respect. The boiling points were 92° to 94° (200 mm.) and 130° to 134° (760 mm.).

0.3395 gave 0.6812 CO_2 and 0.2763 H_2O . $\text{C} = 54.70$; $\text{H} = 9.04$.

Now, had ethyl isopropenyl carbonate been present, it would very probably have been decomposed by the sulphuric acid, but the amount must have been small, since the digestion was stopped and the acid removed on the first indication of the liberation of carbon dioxide. The chief value of this result, however, lies in the fact that it indicates the presence, with the carbonic esters, of condensation products of acetone, which, though readily decomposed by dilute acid, are not so easily removed by phenylhydrazine.

Preparation II.—Since it was possible that digestion with dilute sulphuric acid or even prolonged treatment with phenylhydrazine might bring about the decomposition of ethyl isopropenyl carbonate, a much larger quantity of material was prepared and an attempt was made to isolate the latter ester by repeated fractionation. The product from 300 c.c. of acetone, 32 grams of sodium, and 140 c.c. of ethyl chloro-formate yielded 75 grams of liquid, boiling below 134° , and this, on repeated fractionation under atmospheric pressure, gave two large fractions. The first boiled at 127 — 127.5° , and on analysis:

0.2664 gave 0.5604 CO_2 and 0.2188 H_2O . $\text{C} = 57.37$; $\text{H} = 9.13$;

the other, which boiled at 127.5 — 128.2° , was also analysed:

0.3090 gave 0.6510 CO_2 and 0.2554 H_2O . $\text{C} = 57.44$; $\text{H} = 9.18$.

0.3215 „ 0.6738 CO_2 and 0.2663 H_2O . $\text{C} = 57.15$; $\text{H} = 9.20$;
whilst ethyl isopropenyl carbonate requires $\text{C} = 55.38$; $\text{H} = 7.69$ per cent.

The united liquids were then left in contact with phenylhydrazine for a fortnight, purified as previously described, and repeatedly distilled under atmospheric pressure with a five-section Young's still-head. Four fractions having the following characters were obtained:

Fraction I, 125 — 126° . 0.1570 gave 0.2940 CO_2 and 0.1309 H_2O . $\text{C} = 51.07$; $\text{H} = 8.56$.

Fraction II, 127 — 128° . 0.2552 gave 0.4974 CO_2 and 0.2004 H_2O . $\text{C} = 53.15$; $\text{H} = 8.73$.

Fraction III, 129 — 130° . 0.3138 gave 0.6112 CO_2 and 0.2491 H_2O . $\text{C} = 53.12$; $\text{H} = 8.84$.

Fraction IV, 130 — 132° . 0.3069 gave 0.6067 CO_2 and 0.2482 H_2O . $\text{C} = 53.91$; $\text{H} = 8.99$.

Fraction I was evidently nearly pure diethyl carbonate (b. p. = 126° ; C = 50.85; and H = 8.48 per cent.), and the others appear to consist of diethyl carbonate mixed with ethyl isopropyl carbonate. Freer, who found the vapour density of the fraction $129-130^{\circ}$ to be 4.41, concluded that this was nearly pure ethyl isopropenyl carbonate, but the vapour density of a mixture of diethyl carbonate and ethyl isopropyl carbonate having the composition indicated by the above analysis would have nearly the same vapour density, namely, 4.38.

The fraction $130-132^{\circ}$, containing about 83 per cent. of ethyl isopropyl carbonate and 17 per cent. of diethyl carbonate, should yield 34 per cent. of carbon dioxide on hydrolysis: Freer actually found 33.89 per cent.

Preparation III.—The results just recorded indicate the formation of a large quantity of diethyl carbonate, and on repeating the experiment precautions were taken wholly to remove all alcohol from the ether employed as a diluent.* The acetone was obtained by fractionation of a dried specimen from the bisulphite compound and boiled at $56-56.5^{\circ}$, and the ethyl chloro-formate was dried over phosphorus pentoxide and boiled at 90.5° under 733 mm. pressure. It was found that the yield of liquid boiling at $120-140^{\circ}$ was much reduced, and after treatment with phenylhydrazine was finally resolved by distillation at a pressure of 200 mm. with a three-section Young's still-head into the following portions, each weighing from 2 to 3.2 grams.

(I) B. p. $86-88^{\circ}$. 0.2145 gave 0.4220 CO_2 and 0.1716 H_2O . C = 53.66; H = 8.89.

(II) B. p. $88-90^{\circ}$. 0.1792 gave 0.3570 CO_2 and 0.1467 H_2O . C = 54.04; H = 9.02.

(III) B. p. $90-92^{\circ}$. 0.2319 gave 0.4571 CO_2 and 0.1860 H_2O . C = 53.74; H = 8.91.

(IV) B. p. $92-94^{\circ}$. 0.1868 gave 0.3778 CO_2 and 0.1532 H_2O . C = 55.16; H = 9.11.

(V) B. p. $94-96^{\circ}$. 0.1916 gave 0.3858 CO_2 and 0.1604 H_2O . C = 54.92; H = 9.30.

Assuming that the residue in the still-head had the same composition as the last fraction, the mean percentage of carbon and hydrogen in the fractionated liquid was C = 54.37; H = 9.08 per cent.

In no case, it will be seen, does the amount of hydrogen approach the number calculated for ethyl isopropenyl carbonate, and the analyses

* This is a matter of considerable difficulty unless phosphorus pentoxide as well as sodium is used for the purpose; there can be no doubt that Freer's results also were due to the presence of alcohol in the ether employed by him (*Amer. Chem. J.*, 1893, 15, 590).

indicate that the liquid consisted of ethyl isopropyl carbonate, which appears to decompose slightly on distillation even under reduced pressure into diethyl and diisopropyl carbonates.

Saponification of the Esters.

Fifteen grams of the various fractions boiling under atmospheric pressure from 127° to 133° were saponified on a water-bath with dilute hydrochloric acid, great care being taken that no volatile products escaped. One gram of unsaponifiable oil was obtained, and a liquid which, after drying and distilling, boiled between 78° and 82° and weighed between 9 and 10 grams. Since the theoretical yield of alcohols from 14 grams of mixed esters is about 11 grams, it is evident that acetone has neither been lost nor destroyed during these processes. On fractionating the liquid, no traces of the more volatile substance could be obtained, although every precaution was taken. The results of the fractionation were as follows:

(I) $77.5-79.5^{\circ}$, 4.6 grams; (II) $79.5-80.0^{\circ}$, 1.6 grams; (III) above 80° , 2.5 grams.

An analysis of the first fraction showed that it was pure ethyl alcohol.

0.3270 gave 0.6263 CO_2 and 0.3838 H_2O . C = 52.25; H = 13.04.

$\text{C}_2\text{H}_6\text{O}$ requires C = 52.17; H = 13.04 per cent.

Evidently then the ethyl and isopropyl alcohols obtained are quite free from acetone.

The products of higher boiling point were distilled under a pressure of 30 mm., and the distillate which passed over between 130° and 170° partially crystallised on standing. The semi-solid mass was drained on a porous tile and recrystallised from ether, when a crystalline substance, melting at 177° , was obtained, which volatilised without decomposition under atmospheric pressure. On boiling with soda or baryta, the substance decomposed, yielding carbon dioxide, but the amount available was insufficient for further examination. It crystallised with unchanged melting point after dissolving in ether and treatment with phenylhydrazine.

The molecular weight was determined by the ebullioscopic method, using benzene as solvent.

(I) 0.1975 gram in 12.83 grams of benzene raised the boiling point 0.250° ; molecular weight, 164.4.

(II) 0.3023 gram in 12.83 grams of benzene raised the boiling point 0.354° ; molecular weight, 177.7.

The vapour density was determined by V. Meyer's method, using a hot-air jacket.

(I) 0.1936 gave 22.5 c.c. at 16° and 757 mm.; molecular weight = 208.

(II) 0.1983 gave 23.5 c.c. at 16.5° and 757 mm.; molecular weight = 204.

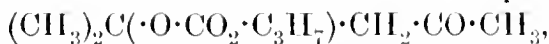
On analysis:

(I) 0.2087 gave 0.4567 CO₂ and 0.1595 H₂O. C = 59.69; H = 8.55.

(II) 0.1657 „ 0.3603 CO₂ „ 0.1278 H₂O. C = 59.86; H = 8.57.

C₁₀H₁₈O₄ requires C = 59.41; H = 8.91 per cent., and molecular weight = 202.

It is probable that this substance is *diacetone isopropyl carbonate*,



since diacetone alcohol, $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, is produced by the action of alkalis on acetone (Koelichen, *Zeit. physikal. Chem.*, 1900, 33, 129).

III. The Action of *p*-Nitrobenzoyl Chloride on "Sodium Acetone."

The difficulty of investigating the action of ethyl chloroformate on "sodium acetone" arose from the fact that the boiling points of the esters formed lie very near the boiling point of mesityl oxide. Their isolation is consequently impossible unless some reagent such as phenylhydrazine is used to remove the mesityl oxide, and it is conceivable that long standing with this substance might decompose ethyl *isopropenyl* carbonate. This difficulty does not arise if the acid chloride employed yields solid esters.

p-Nitrobenzoyl chloride was found to be very suitable, not only on account of its crystalline esters, but because the anhydride is almost insoluble in water and ether, and can be easily separated from the other products of the reaction, consequently allowing a determination of the yield of each product. It was found that the whole of the acid chloride employed was converted into acid anhydride, acid (or sodium salt), and *isopropyl* ester, leaving no possibility of the formation of other compounds. The action of the so-called "sodium acetone" on *p*-nitrobenzoyl chloride therefore consists entirely in the action of caustic soda mixed with some sodium *isopropoxide* on the latter substance. The reaction was carried out under the same conditions as those described by Freer (*Amer. Chem. J.*, 1893, 15, 595) in the case of benzoyl chloride, and the ether, hydrogen, and acetone were purified as previously described. After recrystallising from chloroform, the *p*-nitrobenzoyl chloride, which melted sharply at 73°, was dissolved in four or five times its weight of ether and then added to the "sodium acetone."

Preparation I.—Altogether 20 grams of sodium were dissolved in 200 c.c. of acetone, and 153 grams of *p*-nitrobenzoyl chloride (the calculated quantity is 161 grams) were subsequently added. The "sodium acetone" was cooled by ice-water during the addition of the acid chloride. After long standing in an atmosphere of hydrogen, the products of the reaction consisted of a brown, insoluble substance and a dark ethereal solution with acid properties. The former was a mixture of sodium chloride, sodium nitrobenzoate, and the anhydride of nitrobenzoic acid. The anhydride melted between 175° and 178° , and, after reprecipitation from benzene by light petroleum, consisted of an ochreous, amorphous substance melting from 175° to 179° .

0.4763 gave 37.6 c.c. of moist nitrogen at 15.5° and 736 mm. $N = 8.94$.

p-Nitrobenzoic anhydride, $C_{14}H_9O_7N_2$, requires $N = 8.86$ per cent.

The ethereal solution was freed from nitrobenzoic acid and a little anhydride by repeatedly shaking, first with sodium hydrogen carbonate solution until the latter gave only a faint cloudiness on acidifying, and then with sodium carbonate. Caustic soda was not employed at this stage, as it was conceivable that any unstable ester present might be decomposed by the alkali. The ether was then evaporated from the dried solution, and, after standing some time, brown crystals separated from the oily residue. These were drained at the pump, and about 8 grams of crystals, melting from 95° to 103° , were obtained eventually. The ethereal solution of the crystals was shaken up with 1 per cent. caustic soda solution, which extracted less than 0.6 gram of acid, so that evidently no easily decomposable ester was present. On recrystallisation from ether, the crystals melted between 107° and 108° .

0.1616 gave 0.3479 CO_2 and 0.0820 H_2O . $C = 58.71$; $H = 5.64$.

After sublimation, the crystals melted at 108° .

0.1841 gave 0.3897 CO_2 and 0.0902 H_2O . $C = 57.72$; $H = 5.44$.

*iso*Propyl *p*-nitrobenzoate, $C_{10}H_{11}O_4N$, requires $C = 57.42$; $H = 5.26$.

*iso*Propenyl *p*-nitrobenzoate, $C_{10}H_9O_4N$, „ $C = 57.97$; $H = 4.32$ per cent.

*iso*Propyl *p*-nitrobenzoate was then synthesised by the action of *p*-nitrobenzoyl chloride on potassium *isopropoxide* in order to compare its properties with those of the above substance. After recrystallisation from ether it melted at from 95° to 107° ; after sublimation, at from 107° to 108° ; and on resublimation, at 108° .

0.2166 gave 12.7 c.c. of moist nitrogen at 12.5° and 762 mm. $N = 6.97$.

*iso*Propyl *p*-nitrobenzoate, $C_{10}H_{11}O_4N$, requires $N = 6.70$ per cent.

This places beyond doubt the identity of *isopropyl p*-nitrobenzoate with the only ester obtained by the action of *p*-nitrobenzoyl chloride on "sodium acetone."

Preparation II.—In a second experiment, 10·4 grams of sodium dissolved in excess of acetone were allowed to react with 83·5 grams of *p*-nitrobenzoyl chloride; these proportions differ from those taken in the first experiment only in the fact that in this case the calculated quantity of chloride was used. This was found to make the separation of the various products in a state of comparative purity much easier. Scarcely any sodium *p*-nitrobenzoate was found in the products soluble in water, and the proportion of acid was smaller, and of the anhydride much larger, than in the last case. After the reaction was complete, 59 grams of chloride were recovered as anhydride, 20 grams as acid, and 2 or 3 grams as ester (m. p. 108° after purification), making up altogether 81 to 82 of the total 83·5 grams used. There is no doubt that the remaining 2 or 3 grams can be accounted for by the solubility of the acid in water, some being lost in the aqueous washings, in the sodium hydrogen carbonate, and other solutions after acidifying, and also by the fact that it was impossible to separate the whole of the ester from the condensation products of acetone.

It can therefore be definitely stated that the action of so-called "sodium acetone" on *p*-nitrobenzoyl chloride is no other than that of caustic soda and sodium *isopropoxide* on the latter substance.

With the object of obtaining definite knowledge of the properties of *isopropenyl* esters, and so ensuring their recognition, several attempts were made under varying conditions to prepare *isopropenyl p*-nitrobenzoate by the action of the silver salt on β -bromopropylene, $\text{CH}_3\cdot\text{CBr}\cdot\text{CH}_2$.

In every case a negative result was obtained; a very small quantity of *p*-nitrobenzoic acid was isolated, but nearly the whole of the silver salt remained undecomposed, and no ester could be detected.

This result was not unexpected, as other halogen derivatives of allylene and propylene have been observed by Reboul (*Ann. Chim. Phys.*, 1878, 14, 435) and Oppenheim (*Bull. Soc. chim.*, 1865, [ii], 4, 434) to show similar stability towards silver and potassium salts.

In conclusion, I wish to express my thanks to Dr. Francis, of University College, Bristol, for his advice and suggestions throughout the work.

CXXIX.—*Tetrazoline. Part IV.*

By SIEGFRIED RUHEMANN.

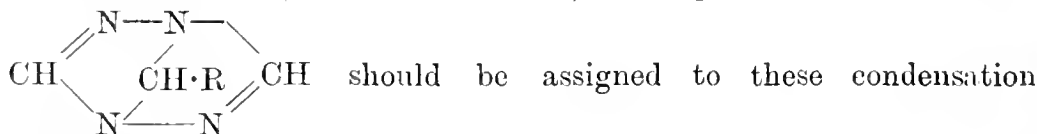
THE properties of the colourless iodide, $C_3H_7N_4I$, and its dark blue periodide, $C_3H_7N_4I_3$, which substances are obtained on digesting tetrazoline with methyl iodide, led Ruhemann and Merriman (*Trans.*, 1905, 87, 1768) to the conclusion that these compounds owed their formation to the following change of the base into its isomeride :



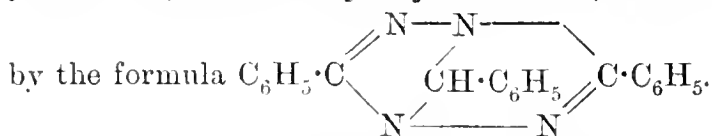
This transformation, which appeared to be supported by the behaviour of tetrazoline towards platinic chloride, was assumed to take place also by the action of aldehydes on the base when compounds were produced, which were represented thus :



Stollé, however (*Ber.*, 1906, 39, 826), is of opinion that the formula



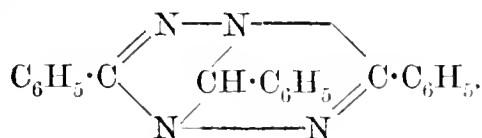
products, because benzaldehyde reacts with *C*-diphenyltetrazoline * to yield benzyldiene-*C*-diphenyltetrazoline, which must be represented



In a recent note (*Ber.*, 1906, 39, 1228) I have pointed out that such a conclusion appears not to be justified on account not only of the facts recorded before by Ruhemann and Merriman (*loc. cit.*), but also owing to the results of the study of *C*-dimethyltetrazoline contained in this paper. Whilst tetrazoline, on treatment with methyl iodide, yields the blue periodide, $C_3H_7N_4I_3$, as well as the colourless iodide, $C_3H_7N_4I$, *C*-dimethyltetrazoline, on treatment with methyl iodide, yields almost exclusively the colourless iodide, $C_5H_{11}N_4I$, which

* I have adopted for the compound $CH \begin{smallmatrix} \diagup N \cdot NH \\ \diagdown NH \cdot N \end{smallmatrix} CH$ the appropriate name tetrazoline, which had been proposed by Pellizzari; accordingly the derivatives with substituents in the imino-groups may be termed *N*-substitution-products, for example, *N*-diphenyltetrazoline, whilst those with substituents in the CH-groups may be indicated by the prefix *C*; for example, *C*-dimethyltetrazoline.

by the action of iodine is transformed into the periodide, $C_5H_{11}N_4I_3$, and this is not blue, but brown. Again, the alkaline solution of the substance $C_5H_{11}N_4I$ does not turn violet on exposure to the atmosphere, as does the iodide, $C_3H_7N_4I$. It follows, therefore, that tetrazoline and *C*-dimethyltetrazoline differ from each other as regards their behaviour towards methyl iodide. A further difference is apparent in the properties of the compounds which these bases yield with aldehydes. It has been mentioned in the previous paper (*loc. cit.*) that an alcoholic solution of a mixture of *C*-dimethyltetrazoline, benzaldehyde, and a few drops of piperidine does not yield a solid product even after several days. I have since found that a condensation product is formed, which is readily soluble in alcohol; the yield, however, is so small that it has not been further examined. Salicylaldehyde condenses with *C*-dimethyltetrazoline more easily, and yields a substance the properties of which are unlike the product of the reaction between the aldehyde and tetrazoline. It contains 1 mol. of water of crystallisation, which it loses at 100° ; it is sparingly soluble in cold dilute hydrochloric acid, and this solution does not give a precipitate with platinic chloride, whilst the corresponding substance, as well as the other condensation products of aldehydes with tetrazoline, are readily soluble in the acid and form platini-chlorides. These facts confirm the view which Ruhemann and Merriman had arrived at in the course of their investigation. It would follow, therefore, that the substances which are obtained by the interaction of aldehydes and *C*-dimethyltetrazoline or its analogues must be expressed by structural formulæ different from those of the corresponding compounds formed from tetrazoline. In view of the facts known up to the present, the formula $R \cdot CH : C \begin{smallmatrix} \text{N}=\text{N} \\ \text{N} \cdot \text{N} \end{smallmatrix} CH$ for the latter compounds appears to be the most probable one; the others, however, for example, benzylidene-*C*-diphenyltetrazoline, are to be represented thus:



Bisdiazomethane, $CH_2 \begin{smallmatrix} \text{N}:\text{N} \\ \text{N}:\text{N} \end{smallmatrix} CH_2$, reacts with aldehydes to yield compounds which, no doubt, have the formula $R \cdot CH : C \begin{smallmatrix} \text{N}:\text{N} \\ \text{N}:\text{N} \end{smallmatrix} CH_2$. These resemble the corresponding derivatives of tetrazoline in their property of being readily hydrolysed; they differ, however, from them inasmuch as their solutions in dilute hydrochloric acid do not yield precipitates with platinic chloride.

EXPERIMENTAL

Action of Methyl Iodide on C-Dimethyltetrazoline.

This reaction takes place on heating the base, dissolved in methyl alcohol, with an excess of methyl iodide in a closed tube at 100°. After six hours' digestion, the tube was opened, when a colourless inflammable gas escaped, which was most probably methyl ether. On evaporating the slightly brown liquid which is formed, an oil remained together with a small quantity of a brown, crystalline solid. This is an additive product of iodine with the iodide, $C_5H_{11}N_4I$, contained in the oil. The latter substance was not isolated, but was transformed into its periodide by mixing the aqueous solution of the oil with a solution of iodine in alcohol. The precipitate which was formed was collected, washed with chloroform, in which it is insoluble in the cold, and crystallised from a hot mixture of methyl alcohol and chloroform. The brown needles which separate on cooling melt at 101°, as previously stated (Ruhemann and Merriman, *loc. cit.*).

0.2042 gave 0.0895 CO_2 and 0.0410 H_2O . $C = 11.95$; $H = 2.23$.

0.2315 „ 22 c.c. moist nitrogen at 18° and 752 mm. $N = 10.86$.

0.2087 „ 0.2886 AgI . $I = 74.71$.

$C_5H_{11}N_4I_3$ requires $C = 11.81$; $H = 2.16$; $N = 11.02$; $I = 75.0$ per cent.

On boiling the periodide with water, it melted, and iodine was liberated, which was removed by distillation with steam. The remaining yellow solution contained the *iodide*, $C_5H_{11}N_4I$; this was not purified, but was transformed into the corresponding *chloride* by boiling the solution with an excess of silver chloride and evaporating the filtrate on the water-bath. The solid residue dissolved in hot alcohol and, on cooling, separated in colourless crystals, which melted at 171—172° and were exceedingly soluble in water. The constitution of the chloride is $CH_2 \cdot C \begin{smallmatrix} \nwarrow N \cdot N(CH_3) \\ \nearrow NH - N \end{smallmatrix} \geq C \cdot CH_3, HCl$; its composition has been verified by a nitrogen-determination of a sample which had been dried at 110°.

0.1908 gave 56.4 c.c. moist nitrogen at 18° and 766 mm. $N = 34.38$.

$C_5H_{11}N_4Cl$ requires $N = 34.46$ per cent.

On mixing concentrated alcoholic solutions of the chloride and platinic chloride, the *platinichloride* is precipitated. It readily dissolves in boiling water and, on cooling, crystallises in orange prisms which melt at 220° with evolution of gas.

0.2473 gave 37 c.c. moist nitrogen at 21° and 752.5 mm. $N = 16.85$,

0.2735, on ignition, left 0.0805 Pt. $Pt = 29.43$.

$(C_5H_{10}N_4)_2, H_2PtCl_6$ requires $N = 16.93$; $Pt = 29.39$ per cent.

The *aurichloride* is formed in yellow needles on mixing concentrated aqueous solutions of the chloride, $C_5H_{11}N_4Cl$, and auric chloride.

0.2560, on ignition, left 0.1083 Au. Au = 42.30.

$C_5H_{10}N_4,HAuCl_4$ requires Au = 42.29 per cent.

The salt readily dissolves in alcohol, especially when hot; it is easily soluble in water, and the yellow solution, on being kept overnight, loses hydrogen chloride and deposits an orange solid.

0.1437 yielded 0.0662 Au. Au = 46.05.

$C_5H_{10}N_4,AuCl_3$ requires Au = 45.83 per cent.

The aurichloride, therefore, is transformed into a double compound of the base, $C_5H_{10}N_4$, and auric chloride, whilst the corresponding platinichloride does not appear to be decomposed in aqueous solution to yield a similar additive product.

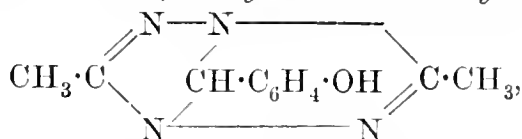
The behaviour of tetrazoline towards platinic chloride, which Ruhemann and Merriman had recorded (*loc. cit.*), has induced me to examine, also, the action of auric chloride towards this base. In this case, I have not been able to obtain the aurichloride, but instead of it the additive compound, $C_2H_4N_4,AuCl_3$, is formed. This is precipitated on adding auric chloride to an aqueous solution of tetrazoline hydrochloride; it is sparingly soluble in alcohol, but insoluble in cold water; it sinters at about 70° and melts at 120° to a deep red liquid.

0.2518 gave 0.1278 Au. Au = 50.75.

$C_2H_4N_4,AuCl_3$ requires Au = 50.70 per cent.

Action of Aldehydes on C-Dimethyltetrazoline.

As stated in the introduction, I have not examined the substance which is formed in small quantity from *C*-dimethyltetrazoline and benzaldehyde. The corresponding product of the reaction between salicylaldehyde and the base, *salicylidene-C-dimethyltetrazoline*,



is produced on adding piperidine (6 drops) to a mixture of the aldehyde (1.7 grams) and the base (1.5 grams) dissolved in alcohol. The solution turns yellow and, in the course of a few hours, sets to a semi-solid mass of crystals. The compound dissolves in hot dilute alcohol and, on cooling, separates in colourless plates which become opaque at 100° and melt at 183° . The substance, dried in a vacuum desiccator over sulphuric acid, gave the following results on analysis:

0.1957 gave 0.4042 CO₂ and 0.1058 H₂O. C = 56.32 ; H = 6.07.

0.1725 „ 36.8 c.c. moist nitrogen at 19° and 746 mm. N = 24.05.

0.1728, on drying at 100°, lost 0.0135. H₂O = 7.81.

C₁₁H₁₂ON₄.H₂O requires C = 56.41 ; H = 5.98 ; N = 23.92 ; H₂O = 7.69 per cent.

Salicylidene-*C*-dimethyltetrazoline is readily hydrolysed by mineral acids ; it is sparingly soluble in cold dilute hydrochloric acid, and this solution does not give a precipitate with platinic chloride.

With cinnamylaldehyde, *C*-dimethyltetrazoline yields, under the same conditions,

Cinnamylidene-C-dimethyltetrazoline.

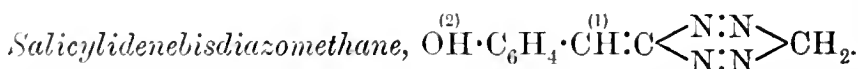
This separates in colourless needles, which readily dissolve in boiling alcohol and melt at 243°.

0.1697, dried at 100°, gave 36.5 c.c. moist nitrogen at 19° and 762.5 mm. N = 24.79.

C₁₃H₁₄N₄ requires N = 24.78 per cent.

Action of Aldehydes on Bisdiazomethane.

Bisdiazomethane was prepared according to Hantzsch and Silberrad's directions (*Ber.*, 1900, 33, 76) by heating ethyl diazoacetate with caustic potash on the water-bath. Several days' digestion is necessary until most of the salt which is first produced has dissolved. The viscous fluid, after washing with alcohol, is mixed with water, and the ice-cold solution carefully treated with dilute sulphuric acid, when tris-bisdiazomethanetetracarboxylic acid is precipitated. The amount of this acid which is formed is very small, but the yield of bisdiazomethane which is produced on melting the acid is almost quantitative. After repeated crystallisation from alcohol, bisdiazomethane melted at 155°. The dihydrotetrazine condenses with only 1 mol. of an aromatic aldehyde, and the reaction takes place on adding a few drops of piperidine to the alcoholic solution of the mixture. The yield of the re-crystallised compounds is unsatisfactory owing to the circumstance that they are hydrolysed with great ease, even by hot water.



The action of piperidine on a mixture of salicylaldehyde and bisdiazomethane, dissolved in alcohol, is accompanied by development of heat. The yellow solution does not deposit a solid until water is added, when the whole sets to a semi-solid mass of crystals. These

are fairly soluble in ether, readily so in alcohol, but insoluble in light petroleum or carbon disulphide; they soften at 175° and melt at 182° .

0.2016 gave 0.4205 CO_2 and 0.0770 H_2O . C = 56.88; H = 4.24.

0.2014 „ 0.4210 CO_2 „ 0.0782 H_2O . C = 57.01; H = 4.31.

0.1780 „ 46.2 c.c. moist nitrogen at 20° and 764 mm. N = 29.84.

$\text{C}_9\text{H}_8\text{ON}_4$ requires C = 57.44; H = 4.25; N = 29.79 per cent.

m-Nitrobenzylidenebisdiazomethane, $(m)\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{C} \begin{smallmatrix} \text{N}:\text{N} \\ \text{N}:\text{N} \end{smallmatrix} \text{CH}_2$.

This substance separates as a white solid from the alcoholic solution of the mixture of *m*-nitrobenzaldehyde, bisdiazomethane, and a few drops of piperidine. The compound is insoluble in cold water or boiling absolute alcohol; it softens at 203° and melts at 211° to a brown liquid. For analysis, it was washed with alcohol and dried in a vacuum desiccator.

0.1840 gave 50.2 c.c. moist nitrogen at 15° and 763 mm. N = 32.08.

$\text{C}_9\text{H}_7\text{O}_2\text{N}_5$ requires N = 32.25 per cent.

I am indebted to the Research Fund Committee of the Society for a grant which has defrayed most of the expense connected with this work.

GONVILLE AND CAHNS COLLEGE,
CAMBRIDGE.

CXXX.—*The Hydrolysis of Ammonium Salts by Water.*

By ERNEST GEORGE HILL.

VELEY has recently described (Trans., 1905, 87, 26) a method by which he attempted to measure the amount of hydrolytic dissociation of aqueous solutions of ammonium salts. The method consisted in boiling the solutions in Jena flasks under an inverted condenser and estimating the loss of ammonia at the end of a given time. The results were not very satisfactory, but the conclusion was drawn that three cases are presented: (1) that hydrolysis may be inappreciable, (2) that it may be dependent on dilution, (3) that it may be independent of the dilution beyond a limiting value. Veley also showed that the extent to which various acids retain ammonia is more or less analogous to their avidity, but that the absolute order of magnitude is not the same in the two cases.

Veley's most striking results were those obtained from the nitrate

and chlorate, which allowed the escape of comparatively large quantities of ammonia, whereas both nitric and chloric acid, being of the same order as hydrochloric, should hydrolyse to a very slight extent. Thus, taking hydrochloric acid as 100, Veley found the avidity of chloric acid to be 6.9, and he omitted nitric acid from the discussion on the assumption that at the temperature of the experiment the nitric acid decomposed and caused secondary reactions. Formic acid also gave anomalous results.

It was suggested by Dr. Veley that measurements of the electric conductivity of the solutions of ammonium salts before and after treatment as in his experiments would give a more accurate means of determining the amount of hydrolysis. A few preliminary experiments showed that this was not so, and that in the case, for example, of ammonium sulphate there was very little change, before or after boiling.

The amount of ammonia escaping is so small, and the ionisation in the solution is so great, that the variation in the conductivity of a normal or fifth-normal solution was almost inappreciable, and the method was abandoned. It seemed, however, possible that if the escaping ammonia could be led into pure water, the conductivity of the water might be used to measure the amount of ammonia evolved. This method proved much more satisfactory.

Estimation of Very Dilute Ammonia by the Conductivity of its Solution.

From the conductivity or resistance curve, it is possible to estimate the amount of ammonia which corresponds to any particular conductivity. Accordingly, if precautions are taken to avoid contamination of the water, it should be possible, by aspirating a current of purified air through a solution containing free ammonia, and passing the ammoniacal air into conductivity water, to obtain a solution of ammonia in water, the conductivity of which is a measure of the ammonia dissolved. The method would be specially applicable when the ammonia to be measured is very small. After a number of experiments with various forms of aspirators, flasks, and absorption vessels, it was found necessary to purify the aspirated air from all carbon dioxide, to secure a uniform rate of flow, to avoid transfer of the ammonia solution from one vessel to another, to avoid condensation of water vapour on the limb of the flask containing the ammonium salt solution, and to measure accurately the ammonia solution before taking its conductivity, also the air passing through the whole apparatus.

These conditions were obtained as follows:

The air was supplied from an ordinary gas holder and was purified

by passing it through a series of wash bottles containing potassium hydroxide solution, and then through a tube containing glass wool moistened with water. The rate of flow was regulated once for all by placing a constricted capillary tube between the purifiers and the laboratory vessel to be described.

The volume of air passed was measured by collecting it, after it had passed through the absorption vessel over water at 15° , in a graduated 800 c.c. flask with a narrow neck. To avoid condensation of water vapour on any part of the apparatus before the absorption vessel, a special form of vessel was designed for containing the salt solutions, every part of which was kept at the temperature of steam, so that no condensation could take place until the air passing through the apparatus had reached the absorption vessel. And lastly, to avoid transfer of solutions and to obviate the difficulty of measuring the volume of the solution before taking its conductivity, the cell itself was graduated and was designed of such a pattern that it served as the absorption vessel.

The Conductivity Cell and Absorption Vessel.

A tube of about 4 mm. cross section, bent twice at right angles, was constricted at the end *D* and sealed into the cell *E*. The constriction was less than 1 mm., the diameter of the cell being about 10 mm. The cell was about 6 cm. long, and at its upper end a tube of 6 mm. diameter was sealed with a slight constriction at the joint. At a distance of 16 cm. from the cell, a small pipette-like bulb was blown as a safety trap for any water forced up the tube, but this was never needed during the experiments. The electrodes were as large as possible and about 5 mm. apart. They were drawn up against the sides of the cell, so as to be quite rigid, and the connecting wire passed into mercury cups bent upwards and extending well above the cell.

The cell was graduated on the two limbs to hold exactly 20 c.c. (see diagram, p. 1277).

The Laboratory Vessel.

This vessel, used for containing the solution of a salt of ammonium during the passage of 800 c.c. of air, was made as follows :

One of the tubes of a 50 c.c. pipette was lengthened considerably and the other was replaced by a narrow tube with a constriction at the entrance to the bulb. This tube was bent twice at right angles, and the end of it (*C*) shaped conveniently as in the figure. The wider tube was bent so as to incline at about 115° to the bulb, and on this was placed a small condenser, the end subsequently being bent downwards

parallel to the bulb. The construction is best shown by the figure. The end *A* was drawn out into a strong, narrow point, which could enter the narrow limb of the conductivity cell. The condenser was kept hot by a supply of steam from a boiler, and the bend of the tube was covered by lengthening the condenser with wide bore rubber tubing cut to shape.

Round the narrow limb of the cell a second steam jacket was placed, so that the latter met the rubber prolongation of the condenser described above. Thus the whole of the limb *B B B* was kept at the temperature of steam. It was therefore no longer possible for any condensation to take place in this limb (see diagram).

The bulb of the pipette was immersed in a very deep water-bath, and the latter was covered with the usual rings and a small cap, which fitted over the ends of the condenser and the side tube *C*. In this way the whole of the laboratory vessel was kept at a high and constant temperature. Owing to the shape of the limb *B B* there could be no spurting of the solution into the cell.

The end of the tube *B B* was connected with the cell by a small piece of rubber tube, which was wired on to the outside of the narrow limb of the cell, the latter being widened for 10 mm. at its end to allow the tube *B B* to enter. This joint was so made that the glass of the two tubes just touched and the rubber came into contact with only the outside of the tubes. The point *A* entered into the limb of the cell for about 8 mm. The cell was immersed in cold water during the experiment.

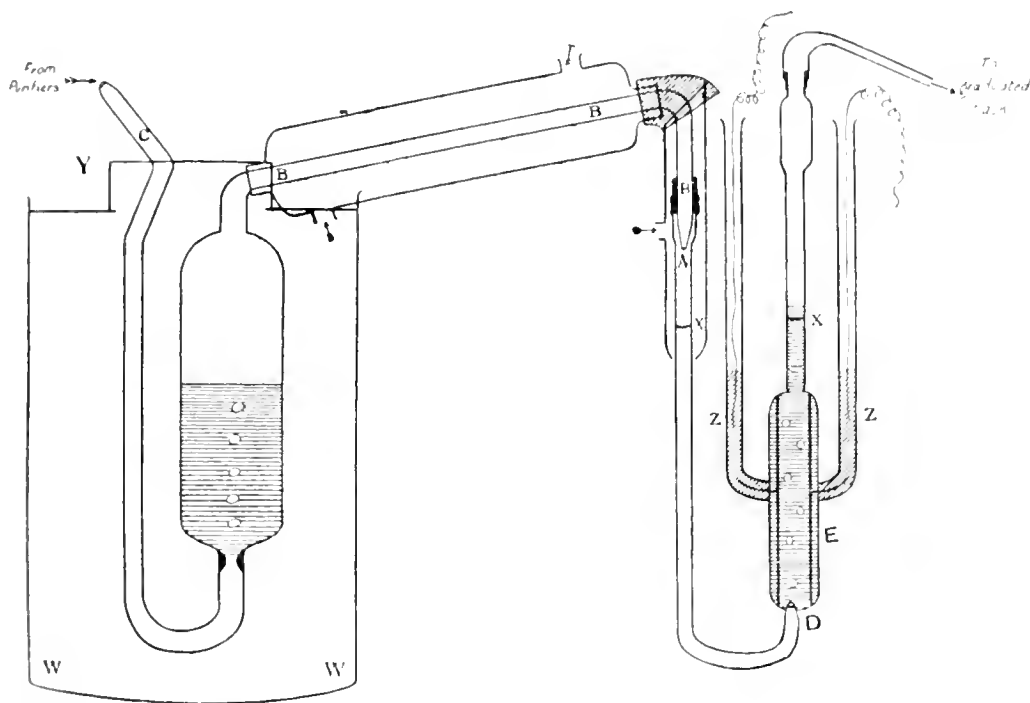
Method of Experiment.

At the beginning of an experiment, conductivity water, prepared as subsequently described, was placed in the cell and its conductivity measured. This was found to be slightly diminished by passing the air, purified as above, through the cell for fifteen minutes. No water was considered suitable which had a greater conductivity than 1.5×10^{-6} units.

A solution of the salt was made in conductivity water in a 200 c.c. flask kept for the purpose. Of this solution, 50 c.c. were withdrawn by a pipette, also kept for this purpose but not specially standardised, placed in a small beaker, and immediately drawn into the laboratory vessel by connecting a rubber tube to *B A* and aspirating the solution through *C*. The rubber tube was then removed and the end of the glass tube *A* rinsed with conductivity water. The laboratory vessel was then placed in the water-bath and joined up with the cell, which contained about 16 c.c. of water at the beginning of an experiment. A bent hood fitted over the top of the cell by means of a rubber collar led by a long delivery tube to the 800 c.c. flask inverted over water,

in which the air passing through the apparatus was collected and measured. The water was always kept at 15° , and towards the end of the experiment the flask was sponged with water at that temperature.

When the connections were made, the boilers and water-bath were heated, and after a few minutes air regulated as previously described was passed until exactly 800 c.c. had been collected in the measuring flask. This took a little less than an hour. The air was then stopped and the cell disconnected. The cell was filled up to the graduation mark with water directly from the conductivity still and placed in the thermostat, which held several gallons of distilled water. It was



W, water-bath; *XX*, graduation mark on the cell; *F*, copper cap fitting over the water-bath rings, with openings for the limbs of the vessel; *ZZ*, mercury cups.

heated to a little above 18° by a current of steam and allowed to cool slowly. When the temperature reached exactly 18° , the conductivity was measured.

With the apparatus above described, sixteen experiments were made with five different concentrations of ammonium sulphate solution. The results were quite satisfactory, the resistances measured differing by less than three per cent. from the mean for a particular concentration. Thus for normal ammonium sulphate the values were 1019, 1027, 1069, 1087, 1083. These were the most discordant results obtained, and a resistance of about 1000 ohms is the least favourable resistance for estimating ammonia by the conductivity method. The

reason is that when the resistance is less than 1000 ohms, the nature of the resistance curve is such that only a small difference in resistance is shown by a comparatively large difference in the ammonia present. In these cases, therefore, the ammonia was estimated by titration. For such determinations the laboratory vessel was used in conjunction with a long test-tube containing a measured quantity of standard acid. The tube was fitted with a doubly-bored rubber stopper, which carried a straight tube passing to the bottom, and a short bent tube, which just passed through the stopper. The long tube was connected with the end *A* of the laboratory vessel, whilst the short end was connected with the delivery tube leading to the collecting flask. The test-tube was rather more than three parts filled with acid. The acid was titrated before and after the passage of 800 c.c. of air, with a very dilute ammonia solution. The latter was standardised for every experiment with standard hydrochloric acid, which also was standardised from time to time with both silver nitrate and sodium carbonate. Experiments were made to ascertain whether a second absorption tube was required, but it was found that one tube of acid, containing 50 c.c. of acid (1 c.c. = 0.000475 gram HCl), absorbed all the ammonia.

With ammonium acetate, the following values were obtained on different days with different solutions.

Grams of ammonia absorbed in the acid :

	<i>N</i> .	<i>N</i> /5.	<i>N</i> /25.
<i>A.</i>	0.0323	0.00861	0.00169
<i>B.</i>	0.0322	0.00816	0.00163

To compare the absorption method with the conductivity method in the least favourable cases of the latter, measurements of *N*/5 salicylate may be quoted.

Two experiments gave 1042 and 1030 for resistances, the mean of these corresponding to 0.00111 gram of ammonia. By the absorption and titration method, the estimated ammonia was 0.001145 gram.

Reduction of Resistances to Percentage of Ammonia.

In order to reduce the numbers obtained for the resistance of the ammonia solution to percentages of ammonia, it was necessary to plot a curve for the specific resistance of dilute ammonia solution, and read off the values corresponding to the specific resistance of the solution.

There are two sets of figures at 25° for the conductivity of ammonia, and a third set at 18°. The first mentioned are by Ostwald (*Allg. Chem.*, 1893) and Bredig (Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*), and the latter by Kohlrausch (Landolt and Börnstein, *Phys. Chem. Tabellen*). For dilutions such as those dealt with in this

paper, these figures do not agree among themselves, and when the curves are plotted side by side it is seen that Kohlrausch's curve and Bredig's curve run parallel, and that when the latter is corrected by the temperature-coefficient for the dilute ammonia, the two curves differ by about 10 per cent., Kohlrausch's figures for the resistance due to a given percentage of ammonia being about 10 per cent. higher than those of Bredig.

Ostwald's curve almost touches Kohlrausch's at 0.025 per cent. ammonia, but then diverges and cuts Bredig's at the point corresponding to 0.0125 per cent. of ammonia.

The difference between these curves was sufficient to make it necessary for the author to determine a curve of resistance for dilute ammonia, and it was obviously most satisfactory to do this part of the work under conditions as similar as possible to those under which the resistances to be converted were obtained.

The method adopted was to pass air through a solution of ammonia in the laboratory vessel, absorb the issuing ammonia in conductivity water in the cell, and determine the resistance. It was found, as will be shown, that the ratio of the escaping ammonia to the total ammonia in the laboratory vessel was constant, and for the conditions of the experiments was 87.5 per cent.

The ammonia solution was prepared by mixing pure ammonium nitrate and a solution of freshly prepared potassium hydroxide in conductivity water in a Jena distilling flask. The arm of the flask passed into an ordinary Jena flask fitted with a doubly-bored rubber stopper, the second hole of which carried a potash tube. A current of washed hydrogen was then passed through the two flasks for several minutes and the distilling flask gently warmed. The ammonia dissolved in the conductivity water, and the distilling flask was removed. The latter was replaced by a burette fitted with a potash tube, and the ammonia solution was drawn up into the burette. It was then titrated against $N/100$ hydrochloric acid. To perform an experiment, a few c.c. of the titrated ammonia solution were run into a small graduated flask containing conductivity water, and the volume was made up to 100 c.c. Fifty c.c. were then introduced into the laboratory vessel, and the other experimental conditions were precisely similar to those already described. During these experiments care was taken to keep the air of the laboratory as free as possible from carbon dioxide.

Two series of experiments with different ammonia solutions were performed. The agreement was satisfactory.

SERIES I.

Ammonia in laboratory vessel.	Resistance in cell.
0.000391	2056
0.000869	1216
0.0001955	2990
0.0000977	4200
0.0003333	2311
0.000189	6601
0.0001075	1077

One c.c. of the ammonia solution in the
burette contained 0.0000782 gram of
ammonia.

SERIES II.

Ammonia in laboratory vessel.	Resistance in cell.
0.000759	1321
0.001518	939
0.000455	1880
0.001897	840

One c.c. of the ammonia solution con-
tained 0.0000759 gram of ammonia.

From these values a curve of resistances of the ammonia in the cell was plotted and used for converting the other resistances into percentages of ammonia. The proportion of free ammonia passing from the laboratory vessel into the cell was stated above to be 87.5 per cent. This was shown as follows.

A solution of ammonia free from carbon dioxide, prepared in the manner previously described, was titrated against standard acid. Of this solution, a measured quantity was run from the burette into a graduated flask and the volume made up to 200 c.c. Fifty c.c. were now drawn into the laboratory vessel and 800 c.c. of air aspirated through it in the usual manner. The issuing air passed through standard acid which was titrated before and after the experiment.

The following experiments were performed :

The original ammonia solution contained 0.001643 gram per c.c.

The standard acid used for absorption was titrated against the original ammonia solution before and after the experiment. Thus the difference between the two values gave the amount of ammonia absorbed by the acid.

Ammonia introduced into the vessel in c.c.	Ammonia passing into the acid in c.c.	Mean.
15.0	13.25 } 13.15 } 13.15 }	13.18
10.0	8.70 } 8.70 }	8.70
5.0	4.35 } 4.40 }	4.375
2.50	2.20 } 2.15 }	2.183
1.25	2.20 } 1.10 }	1.10

The ratio of the ammonia in the vessel to the escaping ammonia absorbed by the acid is consequently :

$$1 : 0.879, 1 : 0.870, 1 : 0.875, 1 : 0.873, 1 : 0.880.$$

The ratio may thus be considered constant, and it may be assumed that 87.5 per cent. of the ammonia passes from the laboratory vessel into the cell under the conditions of the experiments.

Effect of Dissolved Salts on the Escape of Ammonia.

In the hydrolysis of ammonium salts with water, the amount of free ammonia in the salt solution is small compared with that of the total salt dissolved. It was necessary to ascertain what influence the dissolved salt had on the rate of escape of ammonia under the conditions of these experiments. Raoult (*Ann. Chim. Phys.*, 1874, [v], 1, 262), who used strong solutions, states that ammonium chloride decreases the solubility proportionally to the amount present, but that ammonium nitrate has no effect. The latter statement was confirmed by Claus (*Zeit. anorg. Chem.*, 1900, 25, 236).

Perman (*Trans.*, 1902, 81, 482) gives details of two series of experiments, from which he concludes that ammonium chloride may form a complex molecule with ammonia and that the effect of this is to decrease the vapour pressure of the ammonia. He, however, was working with very strong solutions of ammonia (12—15 per cent. NH_3), and his conclusions were derived from a comparison with an ammonia solution containing the same percentage of ammonia and water. If the comparison is made with a solution containing the same mass of ammonia in unit volume, it is seen that the effect of the ammonium chloride is to increase the vapour pressure, or to decrease the solubility to the ammonia. Perman's figures also seem to show that the alteration in vapour pressure increases with the amount of salt in solution.

It was necessary, therefore, to determine what happened with such concentration of salt as the author was using.

To ascertain the effect of ammonium salts on the rate of escape of ammonia from its solutions under the conditions of the author's work, the following experiments were made.

A dilute solution of pure ammonia was prepared, 50 c.c. of this introduced into the laboratory vessel, which, as in all cases, was heated in the water-bath and 800 c.c. of air passed through it, the issuing air and ammonia passing through a tube of standardised acid. The conditions of this experiment were in all respects similar to those previously described. The acid was subsequently titrated with dilute ammonia. In another experiment, a gram-molecular solution of ammonium nitrate was made up in some of the ammonia solution and 50 c.c. of this used in the laboratory vessel, and in a third case ammonium chloride was used.

Two series of experiments with different ammonia solutions, which, accidentally, were of the same strength, gave:

SERIES A.

Fifty c.c. of each solution used.		Standard ammonia required for neutral- ising the acid after passing the air.
Ammonium chloride (10.7 grams in 200 c.c. of ammonia solution).....		44.75 c.c.
Ammonium nitrate (18.0 grams)		44.70 „
Ammonia solution alone		44.70 „
The amount of ammonia required before passing air was		52.70 „

SERIES B.

Ammonium chloride as above	44.70 c.c.
Ammonium nitrate „ „	44.75 „
Ammonia solution alone	44.70 „

It may thus be concluded that the dissolved salts do not exert any influence on the escape of ammonia when the amount of the latter is small compared with that of the dissolved salt.

There seems no doubt, therefore, that the ammonia evolved under the conditions of the author's experiments is a measure of the relative hydrolysis of the salts used.

The Conductivity Water.

The water used in these experiments, both for preparing the solutions of the salts and for the absorption of the ammonia, was made by distilling tap-water (which had been well boiled for ten minutes) through a dilute solution of permanganate acidified with dilute sulphuric acid and then through a solution of permanganate made alkaline with potassium hydroxide. The two permanganate solutions were contained in Jena flasks of 1000 c.c. capacity and were kept about one-third full.

The issuing steam passed through a trap and was finally condensed in a specially kept Jena flask. With this apparatus it was easy to get a sufficient supply of water with a conductivity not greater than 1.5×10^{-6} at 18°.

The cells were standardised by comparison with solutions of potassium and sodium chloride at 18.0°, and the following values were obtained.

Solution.	Cell 1.	Cell 2.
(1) <i>N</i> /50 Sodium chloride	0·09011	0·06609
(2) <i>N</i> /50 Sodium chloride	—	0·06609
(3) <i>N</i> /500 Sodium chloride	0·09025	0·06549
(4) <i>N</i> /500 Sodium chloride	0·09029	—
(5) <i>N</i> /500 Sodium chloride	0·09020	—
(6) <i>N</i> /100 Potassium chloride	0·09031	0·06597
Mean	0·09024	0·06591

Hence the ratio of the cells to one another was 0·09024 to 0·06591, or 1·369 to 1·000. The first three values were determined before the commencement of the work, but the values in experiments (4), (5), and (6) were obtained during the research, (6) being taken on the completion of the experimental portion. The value of the cells had, consequently, not changed during the work.

The Salts.

The salts used were the chloride, chlorate, nitrate, sulphate, oxalate, salicylate, succinate, citrate, benzoate, acetate, and formate. Of these the organic salts were kindly supplied by Dr. Veley, whilst the others were recrystallised from good specimens in the laboratory. An exception must be made in the case of the chlorate, which was prepared from barium chlorate in the usual manner. It gave no trace of chloride after two crystallisations. The organic salts were all recrystallised with the exception of the citrate, and had all been supplied originally by Kahlbaum.

The ammonium acetate was dried over solid potassium hydroxide in an atmosphere containing ammonia gas, after the crystals had been dried as far as possible on blotting-paper.

In addition to the above, fine crystalline specimens of the ammonium salts of monochloroacetic and trichloroacetic acids were prepared. Unfortunately both decomposed under the conditions of the experiment, the former yielding a considerable amount of hydrochloric acid and the latter chloroform.

The Solutions.

The solutions were made by weighing out exact quantities of the salts in a weighed beaker and making up to 200 c.c. with conductivity water. The strengths used were normal, fifth-normal, and twenty-fifth normal. The solutions were always used immediately after being prepared, and the following table gives the measurements obtained.

Salt.	Normal.		0.2 normal.		0.4 normal.	
	Cell 1.	Cell 2.	Cell 1.	Cell 2.	Cell 1.	Cell 2.
Chloride	3550	(2595)	—	3470	—	5549
	—	2120	—	3577	7314	(5345)
Nitrate	3423	(2495)	5198	(3796)	7611	(5559)
	—	2638	—	3602	—	5443
Chlorate	—	2495	—	3569	7156	(5227)
Salicylate	—	—	—	1030	3172	(2317)
	—	—	1427	(1012)	—	2223
Succinate	—	—	—	830	2399	(1752)
	—	—	—	—	—	1639
Formate	—	—	—	—	—	1345
Sulphate	—	1048	2298	(1678)	—	2681
	—	—	—	1662	—	2780

The numbers in brackets are the values for cell 1 divided by 1.369, and hence would be the resistances of the solution in cell 2.

As previously stated, the conductivity method was not accurate when the resistance in the cell was less than 1000 ohms, but in such cases the titration method already described could easily be applied. As an example of two experiments, we have:

Ammonium acetate, $N/1$ solution, 50 c.c. acid used for absorption.

Ammonia solution used for titration, 1 c.c. = 0.00087 gram ammonium hydroxide.

Before absorption, 50 c.c. acid = 114.00 c.c. ammonia, after absorption = (a) 77.30, (b) 76.50, mean = 76.90; hence ammonia absorbed = $37.1 \times 0.00087 = 0.0323$ grams.

By using the above method as a supplement to the conductivity method, the following table was obtained. In it the resistances are converted into ammonia, which is given as the actual amount passing over from the laboratory vessel.

In all cases except that of the chlorate, the values are the mean of at least two concordant results. In the case of the chlorate, the values are for single experiments.

Salt.	$N/1$.	$N/5$.	$N/25$.
Chloride	0.000255	0.000118	0.0000523
Nitrate	0.000243	0.000111	0.0000520
Chlorate	0.000256	0.000119	0.0000559
Sulphate	0.001015	0.000143	0.000213
Salicylate	0.00552	0.00113	0.000301 *
Benzoate	0.01998	0.00378	0.000798
Acetate	0.03230	0.00838	0.00166
Formate	0.01121	0.00225	0.000640 *
Succinate	0.00990	0.00200	0.000420
Oxalate	0.00988	0.00185	—
Citrate	0.01247	0.00574	0.00272
Monochloroacetate	0.0024	—	—

* Values high; obtained by conductivity method; probably slight decomposition and evolution of carbon dioxide, hence lowering the resistance in the cell.

In the case of dibasic acids, half molecular weights were dissolved in a litre of normal solution.

In the preceding table we have several sets of cases. There are monobasic, dibasic, and tribasic acids, and the two former contain both weak and strong acids.

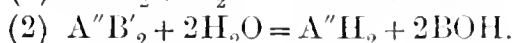
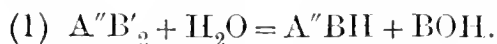
Monobasic Acids.

These form only one simple salt, and consequently only one type of hydrolysis is possible. According as the acid is strong or weak, the equation for the hydrolysis constant will be

$$\frac{C_{\text{AH}} \times C_{\text{BOH}}}{C_{\text{salt}}} = K, \text{ or } \frac{C_{\text{AH}} \times C_{\text{BOH}}}{C_{\text{salt}}^2} = K.$$

Dibasic Acids.

In the case of the salts of dibasic acids, hydrolysis may take place in two ways :



Where the amount of hydrolysis is small, as in the above experiments, it may be assumed that the first of these equations holds, and the equation for the hydrolysis constant becomes $K = \frac{C_{\text{ABH}} \times C_{\text{BOH}}}{C_{\text{salt}}}$ or $K = \frac{C_{\text{ABH}} \times C_{\text{BOH}}}{C_{\text{salt}}^2}$, according as the acid is strong or weak.

These equations may be written $K = \frac{C_{\text{BOH}}^2}{C_{\text{salt}}}$ or $K = \frac{C_{\text{BOH}}^2}{C_{\text{salt}}^2}$ respectively.

If in the above equations we take the ammonia liberated under the conditions of the experiment as C_{BOH} , we have a means for calculating the hydrolysis constant of the solutions used.

In the following table, the equation $K = \frac{C_{\text{BOH}}^2}{C_{\text{salt}}}$ has been used for the first four acids, whilst for the rest, $K = \frac{C_{\text{BOH}}^2}{C_{\text{salt}}^2}$.

Salt.	$K \times 10^5.$			$\sqrt{K} \times 10^4.$		
	N.	N/5.	N/25.	N.	N/5.	N/25.
Chloride	0.00650	0.00690	0.00684	2.55	2.62	2.61
Nitrate	0.00591	0.00605	0.00657	2.43	2.46	2.57
Chlorate	0.00655	0.00708	0.00731	2.56	2.66	2.70
Sulphate	0.103	0.100	0.114	10.15	10.00	10.69
Oxalate	7.74	8.51	—	88.0	92.5	—
Succinate	9.80	10.0	11.0	99.0	100.0	105.0
Formate	12.4	12.6	—	112.1	112.5	—
Benzoate	39.9	34.9	39.8	199.8	189.0	199.5
Acetate	104.0	175.0	172.0	323.0	419.0	415.0
Monochloroacetate	0.576	—	—	24.0	—	—
Salicylate	3.03	3.19	—	55.2	56.5	—

In the foregoing table, the values for K are as constant as can be expected from the experimental method. It may be noted that the nitrate and chlorate behave quite normally, and that the formate gives also a satisfactory result.

The value for the normal solution of the acetate is abnormal. This does not seem to be due to experimental error, since two sets of experiments with different solutions gave concordant results. In this respect, attention may be directed to Veley's figures for the acetate. He found that the normal solution gave a little more than half the percentage of ammonia which was given by 0.2 normal and more dilute solutions, and since the acetate is the salt of the weakest acid used, the figures for this salt should be the most accurate. It therefore appears that in concentrated solution the acetate is proportionately less dissociated.

If we take the inverse of the above figures, we ought to find $1/K$ proportional to the dissociation constants of the acids the salts of which are used, and $\sqrt{1/K}$ proportional to the avidities of the acids obtained by dynamical methods. Since, however, the dissociation constants of the strong acids cannot be used for comparison, we must use the molecular conductivities of their solutions and compare these with $\sqrt{1/K}$. In the following table are given the values for $\sqrt{1/K}$ (hydrochloric acid = 1), also the ratios of the molecular conductivities, and the values for the avidities of the acids obtained from the velocity of decomposition of methyl acetate and the inversion of cane sugar.

Salt.	$\sqrt{1/K}$.	Molecular conductivity.	Inversion of cane sugar.	Decomposition of methyl acetate.
Chloride.....	1.000	1.000	1.000	1.000
Nitrate	1.065	0.991	1.000	0.915
Chlorate.....	0.985	1.000	1.035	0.944
Salicylate	0.046	0.032	—	—
Formate.....	0.023	0.017	0.015	0.013
Benzoate	0.013	0.008	—	—
Acetate	0.006	0.004	0.004	0.0034
Monochloroacetate ...	0.106	0.049	0.048	0.043
Sulphate	0.262	0.625	0.536	0.541
Oxalate	0.029	0.197	0.185	0.174
Succinate	0.026	0.006	0.005	0.005

NOTE.—In the above table, the conductivities for salicylic and benzoic acids which will not form normal solutions have been calculated from their ratios to acetic acid at lower dilutions.

In discussing the above results, we may first take the monobasic acids. Here we find a very good agreement both in order and magnitude with the figures obtained by any of the other methods. The strong acids are almost equal and the ratio of the four weak acids is the same as that of the conductivities. The agreement here is particularly striking, the ratios being :

	Salicylic.	Formic.	Benzoic.	Acetic.
$\sqrt{1/K} \propto$	0.032	0.016	0.0087	0.004
Conductivities	0.032	0.017	0.008	0.004

Or we may compare $1/K$ with the dissociation constants of these acids, in which case, again making the values for salicylic acid the same, we obtain :

	Salicylic.	Formic.	Benzoic.	Acetic.
$1/K \propto$	102	26.0	8.2	1.8
Diss. const. $\times 10^8$	102	21.1	6.0	1.8

Here again the numbers are distinctly of the same order of magnitude. It will be noted in the table, that when hydrochloric acid is taken as the standard for comparison, the weak monobasic acids give slightly higher figures than are given by the conductivities, &c. In this connection it may be suggested that the discrepancy is due to the different temperature-coefficients of strong and weak acids, the conductivities being at 25° and the author's experiments at nearly 100° . It would not appear likely that it is due to experimental error, either in the curve for the resistance of ammonia solutions or in the other observations, since the values obtained for K in the different dilutions are so closely constant.

Dealing next with dibasic acids, we have to remember that, in the hydrolysis of a salt of a dibasic acid, the ammonia neutralising the weaker acid hydrogen is removed first. Thus the method described could not be used to measure the strength of the first hydrogen (or ionisation). That it depends on both the ionisation constants is shown below. With dibasic acids we have :

$$K_1 C_{AH_2} = C_{AH'} \times C_{H'} \text{ and } K_2 C_{AH'} = C_{A''} \times C_{H'},$$

where K_1 and K_2 are the first and second ionisation constants.

Now

$$C_{NH_4^+} + C_{NH_4OH} = C_{A''} + C_{AH'} + C_{AH_2} \quad . \quad . \quad . \quad (1).$$

and (positive = negative charges)

$$C_{NH_4^+} + C_{H'} = 2C_{A''} + C_{AH'} + C_{OH'},$$

where $C_{H'}$ and $C_{OH'}$ are very small and may be neglected, so that

$$C_{NH_4^+} = 2C_{A''} + C_{AH'} \quad . \quad . \quad . \quad . \quad . \quad (2).$$

From (1) and (2) we get

$$C_{NH_4OH} + C_{A''} = C_{AH_2} \quad . \quad . \quad . \quad . \quad . \quad (3).$$

But

$$\begin{aligned} C_{NH_4^+} &= 2C_{A''} + C_{AH'} = 2C_{A''} + \frac{C_{A''} \times C_{H'}}{K_2} \\ &= C_{A''} \left(2 + \frac{C_{H'}}{K_2} \right) \quad . \quad . \quad . \quad . \quad . \quad (4). \end{aligned}$$

Similarly from (1),

$$\begin{aligned}
 C_{\text{NH}_4^+} + C_{\text{NH}_4\text{OH}} &= C_{\text{A}''} + C_{\text{AH}'} + \frac{C_{\text{AH}'} \times C_{\text{H}^+}}{K_1}, \\
 &= C_{\text{A}''} + C_{\text{AH}'} \left\{ 1 + \frac{C_{\text{H}^+}}{K_1} \right\}, \\
 &= C_{\text{A}''} + \frac{C_{\text{A}''} \times C_{\text{H}^+}}{K_2} \left\{ 1 + \frac{C_{\text{H}^+}}{K_1} \right\}, \\
 &= C_{\text{A}''} \left\{ 1 + \frac{C_{\text{H}^+}}{K_2} + \frac{C_{\text{H}^+}^2}{K_1 K_2} \right\} \quad \dots \quad (5);
 \end{aligned}$$

from (4) and (5),

$$C_{\text{NH}_4\text{OH}} = C_{\text{A}''} \left\{ \frac{C_{\text{H}^+}^2}{K_1 K_2} - 1 \right\},$$

and hence

$$\begin{aligned}
 \frac{C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+} + C_{\text{NH}_4\text{OH}}} &= \frac{C_{\text{A}''} \left\{ \frac{C_{\text{H}^+}^2}{K_1 K_2} - 1 \right\}}{C_{\text{A}''} \left\{ 1 + \frac{C_{\text{H}^+}}{K_2} + \frac{C_{\text{H}^+}^2}{K_1 K_2} \right\}}, \\
 &= \frac{C_{\text{H}^+}^2 - K_1 K_2}{K_1 K_2 + K_1 C_{\text{H}^+} + C_{\text{H}^+}^2}.
 \end{aligned}$$

That is, the relative amount of hydrolysis is proportional to a term involving both the first and second ionisation constants.

The Percentage Hydrolysis in Solutions of Ammonium Salts at 100°.

This may be to some degree determined from the above data; thus, in normal ammonium chloride we have 17 grams of ammonia (combined) per litre, and in the laboratory vessel (50 c.c.) we have 0.85 gram. But the free ammonia is 0.000255×1.143 (the inverse of the partition coefficient for ammonia, 0.875).

Thus the percentage hydrolysis is $\frac{100 \times 0.000291}{0.85} = 0.0341$ per cent.

Similarly, for *N*/5 acetic acid we get

$$\frac{0.0323 \times 1.141 \times 100}{0.85} = 4.34 \text{ per cent.}$$

These values are doubtless too high, since, as ammonia is evolved from the solution, hydrolytic action, to a less degree, continues.

They cannot be compared with values obtained by other methods, as the author is not aware of any determined at so high a temperature.

Conclusions.

1. The hydrolysis of ammonia salts with water is in accordance with the laws of mass action for salts of strong and weak acids.

2. This hydrolytic dissociation is inversely proportional to the "strength" of the acid, that is, to the square of the conductivities of solutions of the acid, or their ionisation constants, in the case of univalent acids only.

3. In the case of bivalent acids, the relation between hydrolytic dissociation of salts and the two ionisation constants of the acids is complicated, and the hydrolysis cannot be used as a direct measure of either of the ionisation constants or the "strength" of either of the acid hydrogen atoms in the acid.

4. Certain maximum values are determined for the degree of hydrolysis at 100°.

The author's thanks are due to the authorities of Magdalen College, Oxford, for a grant which covered laboratory expenses, and to Mr. J. J. Manley, the Danbury Curator, for kind assistance in making the apparatus used.

MAGDALEN COLLEGE,
OXFORD.

CXXXI.—*The Action of Nitrous Acid on the Arylsulphonylmetadiamines.*

By GILBERT THOMAS MORGAN and FRANCES MARY GORE
MICKLETHWAIT.

It has been shown previously that the arylsulphonyl derivatives of the aromatic para-diamines, having the general formula, $\text{NH}_2 \cdot \text{X} \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{R}$, give rise to stable diazonium salts, such as $\text{R} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{X} \cdot \text{N}_2\text{Cl}$, which undergo condensation on treatment with aqueous sodium acetate, yielding a diazoimide, $\text{X} \cdot \text{N}(\text{N}_2) \cdot \text{SO}_2 \cdot \text{R}$, where X is the *p*-phenylene group or any of its homologues, and R is an aryl group or a camphor residue. The diazoimides of this series are invariably yellow, and are reconverted into the original diazonium salt by concentrated mineral acids.

The arylsulphonyl-*o*-diamines resemble the mono-acyl and -aryl

derivatives of these bases in yielding diazoimides at once on treatment with nitrous acid even in the presence of concentrated mineral acids. These diazoimides, which are generally colourless, are not attacked by aqueous alkalis or acids.

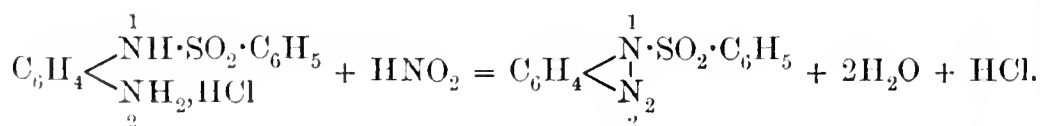
In the experiments described in the present communication, a systematic attempt has been made to ascertain whether this diazoimide condensation occurs among the arylsulphonyl-*m*-diamines, and the compounds examined were the toluene-*p*-sulphonyl derivative of *m*-phenylenediamine and the benzenesulphonyl derivatives of the metadiamines of the toluene, *m*-xylene, and mesitylene series. The case of benzenesulphonyl-*m*-phenylenediamine has been already discussed (Trans., 1905, 87, 83).

The hydrochlorides of these monoacylated metadiamines diazotise readily, forming soluble diazonium chlorides which, on treatment with aqueous sodium acetate, rapidly undergo decomposition even at the ordinary temperature, evolving either the whole or a part of their diazo-nitrogen. When all the diazo-nitrogen is eliminated, the product consists chiefly of the corresponding arylsulphonyl-*m*-aminophenol, and in other instances the residue also contains an ill-defined azo-derivative. In no case has the formation of a diazoimide been observed.

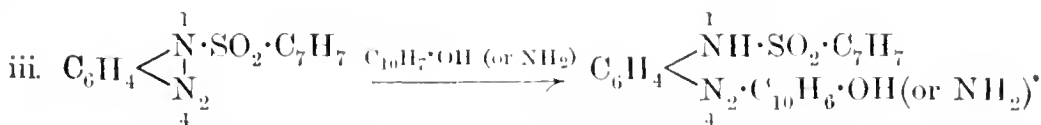
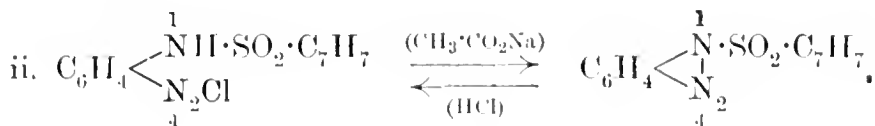
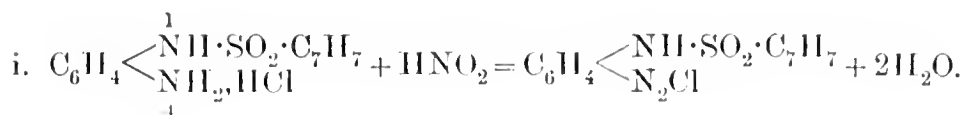
The Action of Nitrous Acid on the Arylsulphonyl-diamines.

The results obtained in the study of the action of nitrous acid on the arylsulphonyldiamines (Trans., 1905, 87, 73, 921, 1302; 1906, 89, 4, 1158) may now be summarised as follows:

1. The arylsulphonyl-*o*-diamines when treated with nitrous acid yield stable colourless *o*-diazoimides without the intermediate formation of any diazonium salt. This condensation occurs even in the presence of strong mineral acids, and the products are not affected by boiling solutions of acids or alkalis.



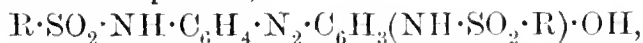
2. The arylsulphonyl-*p*-diamines give rise to stable diazonium salts (i) of the strong acids, but these compounds on treatment with the alkali salt of a weak acid, such as sodium acetate, condense to form *p*-diazoimides (ii). These diazoimides, which are invariably yellow, revert to the diazonium salt under the influence of cold concentrated mineral acids, and combine additively with phenols and aromatic amines to form azo-derivatives (iii).



3. 1:8-Naphthylenediamine resembles the *p*-diamines in this respect, inasmuch as its benzenesulphonyl derivative furnishes a yellow diazoimide which undergoes the above fission with acids, phenols, and amines. This fact indicates that a para-orientation of the NH_2 and $\text{NH}\cdot\text{SO}_2\text{R}$ groups is not an essential condition for the production of a yellow diazoimide of this type.

4. The mixed aliphatic aromatic base, ω -benzenesulphonyl-*o*-aminobenzylamine, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, behaves to some extent like an aromatic arylsulphonyl-*p*-diamine, for it yields stable diazonium salts, and these substances on treatment with sodium acetate give rise to a diazoimide which undergoes fission with acids, phenols, and amines. In one important respect, however, this mixed diazoimide differs from the *p*-diazoimides; it is *colourless*, whereas the latter are all *yellow*. This important distinction shows that the direct attachment of both NH_2 and $\text{NH}\cdot\text{SO}_2\text{R}$ groups to the aromatic nucleus is essential to the development of colour in this series of compounds.

5. The arylsulphonyl-*m*-diamines do not furnish diazoimides; their diazonium salts are stable in solutions of the mineral acids, and in some cases are permanent in the dry state, but on treatment with aqueous sodium acetate they evolve the whole or a portion of their diazo-nitrogen, even at the ordinary temperature, giving rise to arylsulphonyl-*m*-aminophenols, complex hydroxyazo-derivatives, or mixtures of these substances. The lower homologues of the series give chiefly the azo-compounds,



whilst the xylene and mesitylene derivatives furnish the phenolic compounds, $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{X}\cdot\text{OH}$, where X is $\text{C}_6\text{H}_2\text{Me}_2$ or C_6HMe_3 .

6. The benzenesulphonyl derivatives of 1:5-naphthylenediamine and *p*-aminobenzylamine do not yield diazoimides. A small amount of an ill-defined diazo-anhydride was obtained from ω -benzenesulphonyl-*m*-aminobenzylamine, which, however, did not possess the properties characteristic of either the *o*- or the *p*-diazoimides.

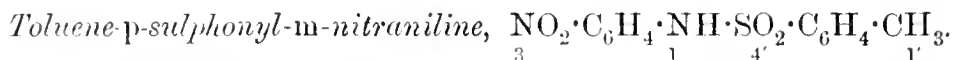
7. In all cases where the formation of a diazoimide occurs, the

hydrogen atom of the arylsulphonamino-group, $\text{NH}\cdot\text{SO}_2\text{R}$, is involved, for when this atom is replaced by a methyl group the production of the diazo-anhydride is entirely prevented.

EXPERIMENTAL.*

1. *m*-Phenylenediamine Derivatives.

The diazonium chloride of benzenesulphonyl-*m*-phenylenediamine has already been shown to decompose under the influence of aqueous sodium acetate in such a way that one molecular proportion of diazo-nitrogen is eliminated from two molecular proportions of the diazo-compound, whilst the residues coalesce to form a complex hydroxyazo-derivative (Trans., 1905, 87, 83).

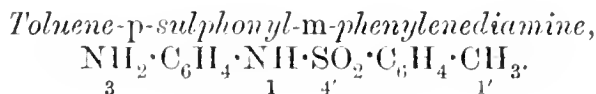


This compound is obtained in quantitative yield by heating together in toluene solution toluene-*p*-sulphonic chloride (1 mol.) and *m*-nitroaniline (2 mols.). After neutralising with sodium carbonate and extracting the excess of *m*-nitroaniline with hot water, the acyl derivative was extracted with aqueous caustic soda and reprecipitated in a granular form by dilute acid. The compound crystallises from dilute alcohol in colourless prisms which acquire a red tinge and melt at 137—138°.

0.1701 gave 0.273 CO_2 and 0.0700 H_2O . $\text{C} = 53.74$; $\text{H} = 4.61$.

$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{C} = 53.42$; $\text{H} = 4.10$ per cent.

This substance is distinctly acidic, as it decomposes sodium carbonate in boiling solutions.



The preceding nitro-compound is readily reduced with iron filings and very dilute acetic acid. When crystallised from water or dilute alcohol, the resulting diamine separates in fine, colourless needles, but when crystallising from strong alcohol it is obtained in larger needles having an orange colour. The substance melts at 143°.

0.3146 gave 29.6 c.c. nitrogen at 21.5° and 759 mm. $\text{N} = 10.68$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 10.68$ per cent.

* The authors desire to record their indebtedness to Messrs. J. M. Hird, F. G. Shepherd, and G. S. Whitby for the preparation of some of the materials required in this research.

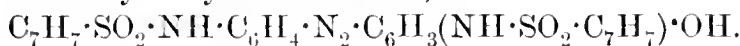
When diazotised in the presence of strong hydrochloric and acetic acids, this base yielded a soluble diazonium chloride, the dilute aqueous solution of which on treatment with aqueous sodium acetate furnished a bright yellow precipitate, which gradually darkened and became brown, while nitrogen was evolved. When this experiment was repeated in the volumeter, the percentages of nitrogen eliminated in two separate decompositions were 5.37 and 5.42, the calculated amount for half the diazo-nitrogen being 5.36. The yellow product changed into a gummy mass on warming with alcohol or benzene; a portion dissolved in the latter solvent, and yellow, nodular crystals mixed with tarry matter were deposited on cooling. A portion was dissolved in warm dilute aqueous caustic soda and the substance reprecipitated from the filtered solution with dilute acetic acid. The pale yellow product melted indefinitely at 110–120° and was analysed with the following results:

0.2568 gave 21.4 c.c. nitrogen at 23° and 762 mm. $N = 9.42$.

0.2558 „ 0.2038 BaSO₄. $S = 10.94$.

C₂₆H₂₄O₅N₄S₂ requires $N = 10.44$; $S = 11.94$ per cent.

These analytical data correspond approximately with the values required for the hydroxyazo-derivative,



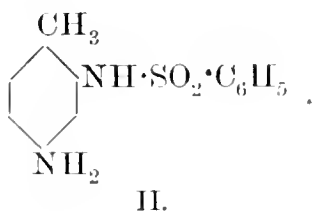
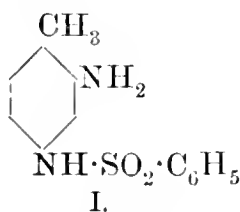
This yellow substance gave no coloration with alkaline β -naphthol either before or after treatment with concentrated hydrochloric acid.

The soluble diazonium chloride obtained in the preceding experiment interacted with β -naphthol in the normal manner; the azo- β -naphthol derivative crystallised from glacial acetic acid in felted masses of scarlet needles and melted at 218.5–219.5°.

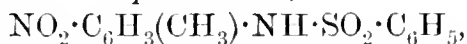
0.2185 gave 20 c.c. nitrogen at 23.5° and 764 mm. $N = 10.33$.

C₂₃H₁₉O₃N₃S requires $N = 10.07$ per cent.

2. 2:4-Tolylene-diamine Derivatives,



Benzenesulphonyl-2-nitro-*p*-toluidine,



which was prepared by heating 2-nitro-*p*-toluidine (2 mols.) with benzenesulphonic chloride (1 mol.) in boiling toluene, was crystallised from alcohol until its melting point became constant at 161°. This

compound has already been described as melting at 160° (*D.R.-P.* 135016; *Chem. Centr.*, 1902, ii, 1166). This patent also contains a description of 4-benzenesulphonyl-2:4-tolylenediamine (I), which can be obtained from the preceding nitro-compound by reduction with iron and very dilute acetic acid. The preparation obtained in these experiments melted at 139° , the patent giving the melting point as 138° .

When diazotised in the presence of strong hydrochloric acid, the base yielded a crystalline diazonium chloride, which dissolved in water to a clear solution. On adding aqueous sodium acetate to this liquid, an intense yellow precipitate was produced, which reddened and evolved nitrogen. When this decomposition was carried out in the volumeter, the amounts of nitrogen evolved varied somewhat in different experiments, being always more than half the theoretical amount, but even on warming to 63° the quantity eliminated still fell short of the total diazo-nitrogen. The residue, which was soluble in caustic soda and reprecipitated by acids, had no definite melting point and appeared to be a mixture of at least two substances, probably a phenol mixed with a hydroxyazo-derivative.

The diazonium chloride when condensed with alkaline β -naphthol gave a cherry-red precipitate of the alkali salt of the azo- β -naphthol derivative; the latter when set free by dilute acetic acid crystallised from glacial acetic acid in scarlet, felted needles and melted at $247-248^{\circ}$.

Benzenesulphonyl-4-nitro-o-toluidine, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_3(CH_3) \cdot NO_2$.

The 4-nitro-*o*-toluidine (m. p. $107-108^{\circ}$) required for these experiments was obtained together with 6-nitro-*o*-toluidine by the nitration of *o*-toluidine in concentrated sulphuric acid and was separated from this isomeride by Green and Lawson's method (*Trans.*, 1891, **59**, 1031). The purified base was boiled with benzenesulphonic chloride in toluene solution for three hours; the residue after evaporating to dryness was extracted repeatedly with aqueous sodium carbonate, the unchanged amine allowed to crystallise, and the alkaline filtrate acidified with dilute hydrochloric acid. When recrystallised from dilute alcohol, the benzenesulphonyl derivative separated in colourless, pearly leaflets melting at 172° .

0.3078 gave 26.0 c.c. nitrogen at 21° and 764 mm. $N = 9.67$.

$C_{13}H_{12}O_4N_2S$ requires $N = 9.58$ per cent.

2-Benzenesulphonyl-2:4-tolylenediamine (Formula II).

The preceding nitro-base, when reduced with iron and dilute acetic acid, yielded the corresponding diamine, which was extracted with alcohol from the iron oxide precipitate and recrystallised from the

same solvent with the addition of animal charcoal. It separated in colourless leaflets and melted at 138° .

0.1896 gave 17.6 c.c. nitrogen at 21° and 767 mm. $N = 10.66$.

$C_{13}H_{11}O_2N_2S$ requires $N = 10.68$ per cent.

When added to strong hydrochloric acid, the base at first became viscid and then formed the crystalline hydrochloride. The mixture when thoroughly cooled and diazotised yielded a crystalline diazonium chloride, which was soluble in water to a clear solution. When mixed with sodium acetate, this liquid became turbid, yielding a yellow precipitate which darkened and evolved nitrogen; 9.98 per cent. of gas was evolved at the ordinary temperature, the calculated percentage of diazo-nitrogen being 10.68.

The product was a somewhat ill-defined substance which did not crystallise readily from alcohol or benzene, but dissolved in aqueous caustic soda and was reprecipitated by dilute acetic acid; a portion which had been thus treated melted at 183° and was taken for analysis:

0.1776 gave 9.4 c.c. nitrogen at 23° and 762 mm. $N = 5.98$.

0.3062 „ 0.2714 $BaSO_4$. $S = 12.16$.

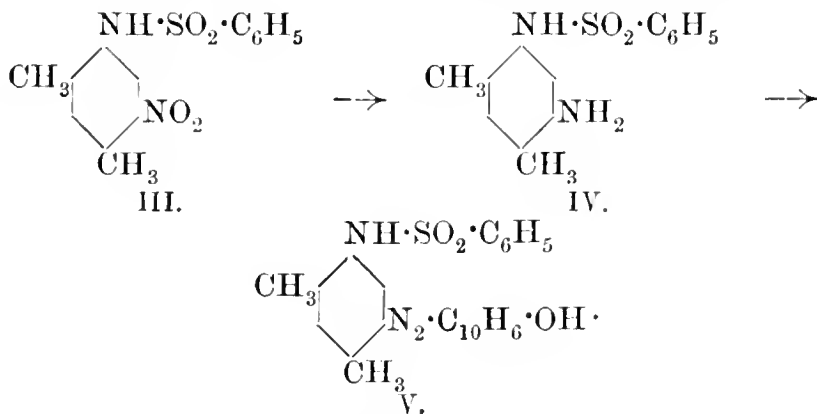
$C_{13}H_{13}O_3NS$ requires $N = 5.32$; $S = 12.16$ per cent.

These results agree fairly well with the composition of a benzenesulphonylamino-*p*-cresol having the formula



The diazonium chloride of 2-benzenesulphonyl-2:4-tolylenediamine when condensed with alkaline β -naphthol yielded the brownish-red alkali derivative of an azo-compound. The azo- β -naphthol, when set free with dilute acetic acid, crystallised from glacial acetic acid in orange-red needles melting at 208° .

[With E. G. COUZENS.]—3. 4:6-Diamino-*m*-xylene Derivatives,



4:6-Dinitro-*m*-xylene was prepared in the manner already indicated (Trans., 1902, 81, 92), crystallised repeatedly to free it from its

isomeride, 2 : 4-dinitro-*m*-xylene, and reduced with alcoholic ammonium sulphide. For this purpose the dinitro-compound was dissolved in boiling alcohol, aqueous ammonia added, the solution saturated with hydrogen sulphide, and then boiled in a reflux apparatus for fifteen minutes. More ammonia was then added and the saturation with hydrogen sulphide repeated until a considerable amount of yellow precipitate had separated. The solution was then evaporated down with water and the total residue extracted with dilute hydrochloric acid ($\text{HCl} : \text{H}_2\text{O} = 1 : 1$); the nitroxyldine was precipitated in the filtrate with ammonia and recrystallised from alcohol. By working with 10 gram batches, about 8.5 grams of the nitro-base were obtained in each operation. After several crystallisations from alcohol, the 6-nitro-*m*-4-xyldine melted at 123° .

Benzenesulphonyl-6-nitro-m-4-xyldine (III) was readily obtained by adding benzenesulphonic chloride to the foregoing nitro-base dissolved in dry pyridine and heating the solution in a reflux apparatus for about two hours. The mixture, which had then become black and tarry, was poured into cold dilute hydrochloric acid, allowed to remain overnight, and then extracted with boiling sodium carbonate solution, the benzenesulphonyl derivative being reprecipitated with dilute acid. This product was repeatedly crystallised from alcohol, when it separated in colourless, prismatic crystals melting at 148.5° .

0.2972 gave 25.3 c.c. nitrogen at 23° and 764 mm. $\text{N} = 9.61$.

$\text{C}_{14}\text{H}_{14}\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 9.15$ per cent.

4-Benzenesulphonyl-4 : 6-diamino-m-xylene (IV).—The reduction of the preceding nitro-compound, which was effected in the usual way with iron and dilute acid, gave an almost quantitative yield of the corresponding diamine, which was extracted from the iron oxide precipitate with alcohol. When recrystallised from this solvent, the base separated in colourless leaflets melting at 167° .

0.1546 gave 14.1 c.c. nitrogen at 23° and 766 mm. $\text{N} = 10.36$.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 10.14$ per cent.

Diazotisation Experiments with 4-Benzenesulphonyl-4 : 6-diamino-m-xylene.

1. *Azo-derivative*.—The base when diazotised in the usual way yielded a soluble diazonium chloride which, when condensed with β -naphthol in alkaline solution, furnished the slightly soluble alkali salt of the azo- β -naphthol. The latter was set free with dilute acetic acid and crystallised from benzene.

0.1804 gave 15.4 c.c. nitrogen at 22° and 762 mm. $\text{N} = 9.71$.

$\text{C}_{24}\text{H}_{21}\text{O}_3\text{N}_3\text{S}$ requires $\text{N} = 9.74$ per cent.

Benzenesulphonyl-4-amino-m-xylene-6-azo-β-naphthol (V) separated in small, scarlet needles melting at 241°.

2. *Decomposition of the Diazonium Salt*.—Weighed quantities (about 0·3 gram) of the base were diazotised in moderately strong hydrochloric acid and mixed in the volumeter with excess of sodium acetate. About two-thirds of the diazo nitrogen were evolved at the ordinary temperature after twelve hours, and the remainder was eliminated on gently warming. In two separate experiments, the percentages of nitrogen liberated were 9·86 and 9·95, the calculated value for total diazo-nitrogen being 10·15. The residue was a yellow, viscid mass, which hardened on cooling; it was soluble in caustic soda and reprecipitated by acids, and had the properties of the following acylaminophenol, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_2(CH_3)_2 \cdot OH$. As it did not crystallise readily from anhydrous solvents (benzene, petroleum, &c.), the product (m. p. 136—143°) was analysed without further purification.

0·3092 gave 15·7 c.c. nitrogen at 22° and 763 mm. $N = 5·77$.

0·3504 „ 0·2918 $BaSO_4$. $S = 11·43$.

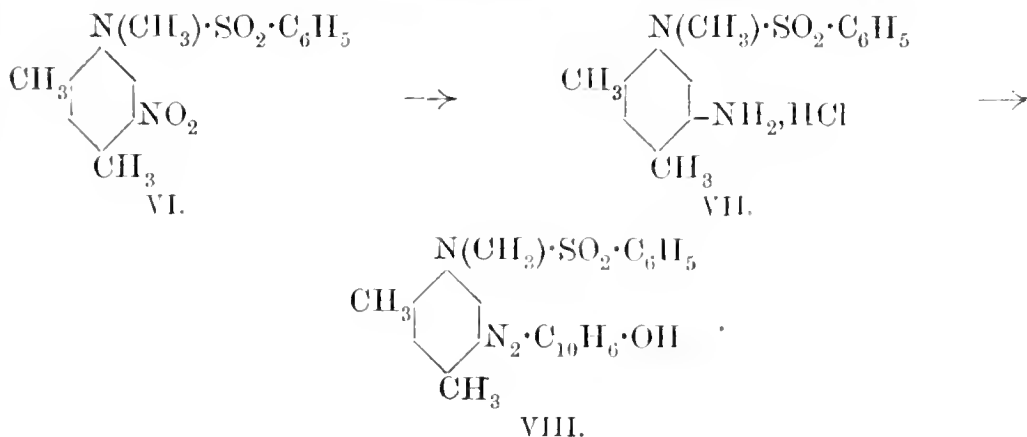
$C_{14}H_{15}O_3NS$ requires $N = 5·04$; $S = 11·56$ per cent.

This phenolic substance was subjected to the Schotten-Baumann reaction, and the product, which did not crystallise readily, was ultimately obtained from a mixture of water and alcohol in light yellow flakes melting indefinitely at 179—182°.

0·2584 gave 7·8 c.c. nitrogen at 23° and 760 mm. $N = 3·40$.

$C_{21}H_{19}O_4NS$ requires $N = 3·67$ per cent.

as-(4)-*Benzenesulphonylmethyl-4:6-diamino-m-xylene*,



Benzenesulphonylmethyl-6-nitro-m-4-xylylidine (VI) was readily obtained by methylating benzenesulphonyl-6-nitro-*m*-4-xylylidine in absolute alcohol with methyl iodide and caustic soda; it crystallised from the same solvent in well-defined colourless prisms melting at 185—186°.

0.2990 gave 23.3 c.c. nitrogen at 22° and 763 mm. $N = 8.86$.

$C_{15}H_{16}O_4N_2S$ requires $N = 8.75$ per cent.

The reduction of this nitro-compound with iron and dilute acetic acid led to the production of an oily base which was extracted by alcohol from the iron oxide precipitate. As this oil could not be induced to solidify, its hydrochloride was prepared and recrystallised from water acidified with hydrochloric acid; the salt separated in colourless leaflets, decomposing indefinitely at about 160°.

0.1900 gave 13.9 c.c. nitrogen at 21° and 762 mm. $N = 8.35$.

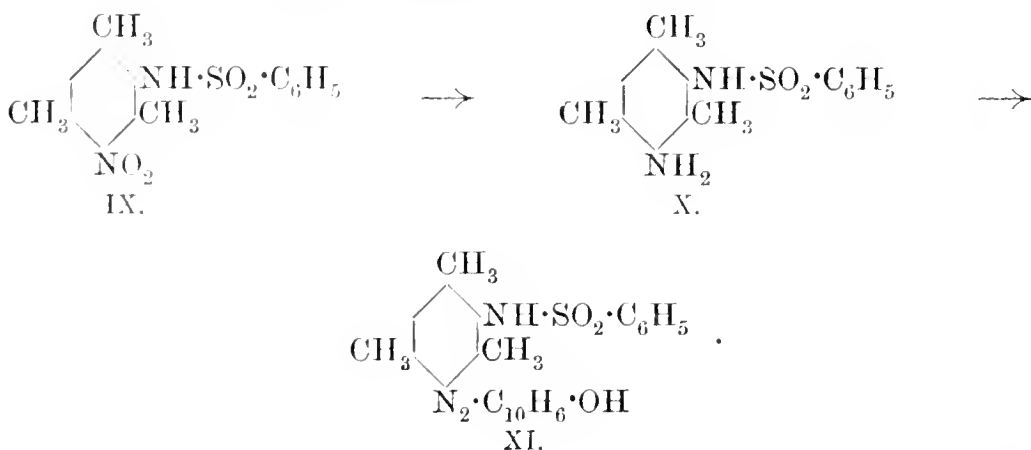
0.4858 „ 0.2078 AgCl. $Cl = 10.60$.

$C_{15}H_{19}O_2N_2SCl$ requires $N = 8.56$; $Cl = 10.87$ per cent.

as-(4)-*Benzenesulphonylmethyl-4 : 6-diamino-m-xylene hydrochloride* (VII) diazotised readily to form a soluble diazonium chloride which, when treated in the volumeter with cold aqueous sodium acetate, decomposed very slowly, evolving only about one-sixth of its diazo-nitrogen after twelve hours. On warming the mixture to 60°, a further portion of the diazo-nitrogen was eliminated. A nitrogen estimation in the dark red residue indicated that it was a mixture of a phenolic substance with a hydroxyazo-derivative.

Benzenesulphonylmethyl-4-amino-m-xylene-6-azo-β-naphthol (VIII) was prepared from the foregoing diazonium salt and β-naphthol and recrystallised from glacial acetic acid or benzene, when it separated in hard, nodular, scarlet crystals melting above 260°.

4. Diaminomesitylene Derivatives,



Dinitromesitylene was prepared by Fittig's method and reduced with equal weights of iron filings, glacial acetic acid, and ten parts by weight of water; the mixture was boiled vigorously for an hour, rendered alkaline with sodium carbonate, and filtered rapidly, when

yellow needles of nitromesidine separated. A further quantity may be obtained on concentrating the mother liquors, or these may be treated with benzenesulphonic chloride and caustic alkali.

Benzenesulphonylnitromesidine (IX). — Nitromesidine interacts readily with benzenesulphonic chloride either in boiling toluene or pyridine solution, and the condensation can also be effected by the Schotten-Baumann reaction. As prepared in this way, benzenesulphonylnitromesidine is contaminated with a certain amount of *s*-dibenzenesulphonyldiaminomesitylene, $C_6H(CH_3)_3(NH \cdot SO_2 \cdot C_6H_5)_2$, owing to the presence of diaminomesitylene in the product of the reduction of dinitromesitylene. The two benzenesulphonyl derivatives were separated by their different solubilities in dilute alcohol, the disulphonyl derivatives separating first as the solution cooled. After recrystallisation from the same solvent, the disulphonyl derivative melted at 248° .

0.3719 gave 22.2 c.c. nitrogen at 20° and 760 mm. $N = 6.83$.

0.2584 „ 15.2 c.c. „ „ 21.5° „ 759.5 mm. $N = 6.70$.

0.3692 „ 0.4022 $BaSO_4$. $S = 14.99$.

$C_{21}H_{22}O_4N_2S_2$ requires $N = 6.50$; $S = 14.83$ per cent.

The dilute alcoholic filtrate from the *s*-dibenzenesulphonyldiaminomesitylene yielded on evaporation striated, yellow leaflets, but when recrystallised from benzene the substance was obtained in the form of colourless, nodular crystals melting at $162-163^\circ$.

0.1262 gave 10.0 c.c. nitrogen at 23.5° and 761 mm. $N = 8.94$.

$C_{15}H_{16}O_4N_2S$ requires $N = 8.75$ per cent.

Benzenesulphonyldiaminomesitylene (X) was obtained from the preceding nitro-compound by reduction with iron filings and dilute acetic acid. The base when recrystallised from dilute methyl alcohol separated in nodular crystals melting at 156° .

0.1558 gave 12.1 c.c. nitrogen at 22° and 762.5 mm. $N = 8.83$.

0.5270 „ 0.4161 $BaSO_4$. $S = 10.84$.

$C_{15}H_{18}O_2N_2S$ requires $N = 9.06$; $S = 11.03$ per cent.

When diazotised in hydrochloric acid, the diamine furnished a colourless solution which, on treatment with sodium acetate, evolved a considerable amount of nitrogen even in the cold. At the same time, a colourless precipitate slowly separated; this substance, which dissolved in aqueous caustic alkalis, but was insoluble in acids, crystallised from dilute alcohol in colourless needles melting at $178-179^\circ$.

0.2938 gave 13.5 c.c. nitrogen at 23° and 760 mm. $N = 5.17$.

$C_{15}H_{17}O_3NS$ requires $N = 4.89$ per cent.

This result indicates that the substance is a benzenesulphonylamino-mesitol, having the formula $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H(CH_3)_3 \cdot OH$.

Benzenesulphonylamino mesityleneazo- β -naphthol (XI), obtained from diazotised benzenesulphonyldiaminomesitylene hydrochloride, crystallised from glacial acetic acid in coppery-red, acicular prisms and flattened needles which melted at 222° .

0.1688 gave 13.8 c.c. nitrogen at 23° and 761 mm. $N = 9.23$.

$C_{25}H_{23}O_3N_3S$ requires $N = 9.43$ per cent.

The sodium salt of this azo-derivative is a deep red substance which is precipitated on warming the alkaline solution containing its generators.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partially defrayed the expenses of this communication.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.



P. S. Clune

CLEVE MEMORIAL LECTURE.

DELIVERED ON JUNE 21ST, 1906.

By THOMAS EDWARD THORPE, C.B., F.R.S.

No circumstance in the national and personal history of experimental science is more remarkable than the position which Sweden and the Swedes occupy in relation to chemistry. When regard is had to her position among Continental nations—to her chequered political history, to her geographical isolation, the comparative sparseness of her population, her relative poverty, the fewness of her seats of learning—the influence which Sweden has been able to exert on the development of that branch of science which it is the proper function of this Society to foster must always excite our wonder, admiration, and gratitude. The mere mention of the names of Bergmann, Scheele, Berzelius, Mosander, Gadolin, Nilson, is sufficient to remind us how great have been her services to the science of chemistry.

In Per Theodor Cleve, who was elected a Foreign Member of this Society in 1883, we had a man who throughout a strenuous life, wholly devoted to academic pursuits, and to the cultivation of pure science, worthily upheld and handed forward the traditions which his countrymen had succeeded in associating with his calling and particular office. In compliance with our custom, and at the request of the Council, I am privileged this evening to offer you some account of the life work of our deceased Foreign Member.

I owe the invitation doubtless to the circumstance that I enjoyed the personal acquaintance and friendship of Cleve, who for some years past did me the honour to accept of my hospitality during his visits to London. Although I had thereby opportunity of learning at first hand something of his personal history and of his achievements, and of noting his mental and intellectual characteristics and of forming impressions such as can only be acquired by social intercourse and personal contact, I am conscious that my account of the man and of his work owes whatever of completeness it may possess to the assistance which has been afforded to me in its compilation by Cleve's daughter and her husband. On learning of the duty which had been imposed upon me by your Council, Dr. and Mrs. Euler were good enough to forward to me an advance copy of the obituary notice which they were preparing for the *Berichte* of the German Chemical Society, and which has now been published. Of this account I have, with their permission, made full use in putting together what I have to tell you this evening.

Per Theodor Cleve was born in Stockholm on February 10th, 1840. He was the thirteenth child of the merchant F. T. Cleve, whose ancestors had emigrated from Western Germany and settled in Sweden during the middle of the eighteenth century. It is told of the young Cleve that even during his school-time his leaning towards natural science, and especially towards natural history, was strongly marked, and that he spent hours which should have been devoted to classical studies in rambling round the country in search of animals, plants and stones—to the despair of the philologists, who set him down, as they had previously done his great countryman Berzelius, as a youth of very little promise. This love for natural history was an abiding passion with Cleve, and constantly struggled with, and in the end conquered, his allegiance to chemistry. Destiny, indeed, intended that he should be a naturalist: the stress of circumstance only made him a chemist. The boyish love of rambling strengthened into a constant yearning for foreign travel. His sympathy with the natural objects around his home—with the birds and flowers of his native woods and fields, and the many wonderful minerals in his native rocks—grew into an intense desire to see and to know Nature in her every mood, and under many skies. Had fortune favoured him Cleve would probably have followed in the footsteps of Humboldt and Darwin, and spent his life in scientific travel; compelling circumstances kept him for the most part at home, and in the end made him what he was.

Although it is clear that Cleve's predilections were towards an academic life, it is not very obvious why he became a chemist. It may have been that the outlook as regards natural history was not very hopeful: Scandinavia forty years ago was not as convinced as now of the supreme importance to her national prosperity of those studies to which Cleve was inclined. As regards chemistry the times were more propitious. The early 'sixties was a period of great unrest in that science, and, as we all know, it culminated in nothing less than a revolution. Although speculation and theory had never much attraction for Cleve, the young *candidat* could not have been wholly uninfluenced by the movement of the time, or insensible to the effect it was exerting on the development of chemistry. Be this as it may, Cleve, who after five years' residence at Upsala had taken his degree, became when twenty-three years of age a lecturer on Organic Chemistry in the University. At that time the Chair on General Chemistry at Upsala was held by Lars Svanberg, who almost exclusively occupied himself with mineralogical inquiries. He was a fairly prolific contributor to the literature on mineral chemistry of the period, and occasionally associated himself with his students in mineral analyses, but Cleve apparently

owed little to his teaching and still less to his example or encouragement.

Cleve's earliest contribution to chemical literature, made when he was twenty-one years of age, was "On Some Ammoniacal Chromium Compounds," and consisted in an extension of the work of Frémy, by whom this interesting class of substances was first made known. The chromammonium derivatives are among the most complicated and perplexing of inorganic compounds, and their discovery undoubtedly gave a great extension to the conception of isomerism in mineral chemistry. Cleve thus early entered on a field of inquiry which occupied him for several years, and which has taxed the energies of many successive investigators, notably Jörgensen and Christensen. Cleve's first communication definitely established the existence and fixed the composition of the initial member of the chromtetrammonium series, namely chlorochromtetrammonium chloride, $\text{Cl}_2 \cdot \text{Cr}_2 \cdot 8\text{NH}_3\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, or, as he termed it, *tetramminchromchlorid*, a salt forming beautiful deep red trimetric crystals.

The study of isomerism, using that term in its widest sense, and the influence of structure and constitution on the properties of bodies, may be said to have been the guiding principle which actuated the major part of Cleve's experimental labours, whether in inorganic or organic chemistry. The most cursory inspection of his published work shows that this was the dominant, underlying motive of his inquiries—the silver thread which ran, as it were, through the fabric he elaborated. This fact requires to be borne in mind, in justice to Cleve, as indicating his philosophic habit of mind, and the real objective of his intellectual activity. Accident and opportunity no doubt at times appeared to change the main current of his thoughts; his mind was too active not to perceive and even occasionally to follow the many side-issues to which his inquiries gave rise, but with a true economy he invariably returned to what he recognised to be the proper direction of his energies. Singleness of aim and tenacity of purpose are the hall-marks of every successful prosecutor of scientific inquiry, and Cleve possessed these characteristics in an eminent degree.

His work on the chromammonium compounds naturally led him to undertake the investigation of similar groups of inorganic substances, in the hope of further elucidation of the problems in which he was interested, and he next occupied himself with the study of the platinum bases, the chemistry of which was even in a more chaotic condition than that of the more recently discovered chromium compounds. The history of the platinum bases, or platinammines, takes its rise from the discovery by Magnus

in 1828 of the famous "green salt" with which his name is associated, and which he prepared by the action of aqueous ammonia on platinous chloride. Ten years later, Gros, under Liebig's direction, obtained a series of chlorinated derivatives of this salt, containing the group NO_3 , and shortly afterwards Reiset prepared the base $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$, of which the compounds prepared by Gros and the green salt of Magnus were regarded as salts.

The relation between these substances was expressed as follows:—

Reiset's first base	$\text{Pt}(\text{NH}_3)_4(\text{OH})_2$.
Gros's salt	$\text{Cl}_2\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$.
Green salt of Magnus.....	$\text{Pt}(\text{NH}_3)_4 \cdot \text{PtCl}_4$.

In 1844 Reiset obtained a second series of salts containing only half as much ammonia as the first series, and from which a new base could be prepared—the so-called Reiset's second base. Peyrone some time afterwards prepared a chloride which had the same composition as the chloride of Reiset's second base, namely, $\text{PtCl}_2 \cdot 2\text{NH}_3$, but which was altogether different from it in properties. Isomerism among inorganic substances was at that time unknown, and to Berzelius, who first gave us the term, was inconceivable. Personal friendship and trust in Wöhler may have predisposed him in the first instance to tolerate the existence of isomerism among carbon compounds, to which his own work on tartaric acid may have further inclined him, as something exceptional and peculiar to organic substances, but, in the main, to Berzelius identity of composition meant identity of character: there was no room in his system for inorganic isomerides, and Peyrone's discovery was met by flat incredulity. But evidence as to its truth steadily accumulated. Raewsky discovered the analogues to Gros's compounds, and Gerhardt and Laurent made known the existence of the platinamine salts. The theoretical aspect of these facts was everywhere recognised as of the highest importance. They constituted so many test cases by which the sufficiency of a doctrine which had long dominated chemistry could be tried, and served to augment the slowly accumulating body of testimony which eventually overthrew it. Driven to recognise the existence of these compounds, Berzelius made futile efforts to reconcile them with his electro-chemical system. But the inadequacy of these attempts was apparent to all but the blindest adherents of the Swedish school. On the other hand, Gerhardt, by an extension of the theory of types, gave a more or less plausible explanation of the mode of structure and constitution of these groups of substances, which was not out of harmony with prevalent conceptions, and which, indeed,

in some respects, foreshadowed present-day developments in its recognition of variable valency. But the swing of the pendulum is not confined to that particular department of intellectual activity we call politics; we have constant examples of it in every sphere of human thought, for the movement is eventually controlled and regulated by the gravitational tendency which is inherent in the truth itself. The explanations of Berzelius might be partial and imperfect, but the underlying truth in his doctrine could never be wholly obscured, and when the system of types, as a theory of chemistry, in its turn gave way to a more rational generalisation, what there was of permanent value in both became incorporated in the new philosophy.

As I have said, the theoretical significance of these compounds was very generally recognised, and in this connection I may recall the early work of Buckton, extending from 1851 to 1854, and of Hadow, published in our Journal for 1866.

It was at about this period that Cleve undertook the study of the ammonia platinum compounds. He had, of course, been reared under the doctrine of Berzelius, whose influence, indeed, was paramount in Sweden long after it had waned in the rest of Europe, and he had no disposition or inducement at the time to trouble himself about its limitations. Speculative chemistry had never, at any period, much attraction for Cleve. In this respect he resembled Bunsen, with whose mental characteristics he had other points of resemblance and sympathy. His first papers on the platinum bases, published by the Royal Society of Sciences of Upsala, are, therefore, as might have been anticipated, written wholly in the spirit and from the standpoint of an adherent of the orthodox school of chemical philosophy in Sweden. He was induced, he says, to undertake the investigation of these substances as a sequel to his work on the chromammonium compounds in the hope of eventually obtaining an independent view of the general constitution of the metal-ammonia compounds. The first object of his inquiry was sufficiently modest; it was to determine the position of the chlorine in the salts obtained from Gros's base. Gros's base he found to be free from halogen; it could be regarded as an oxidised derivative of Reiset's first base. The salts obtained by Gros, as well as those of Raewsky, were, in fact, derivable from the hydroxyl compound

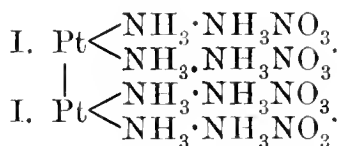


a formula which further serves to indicate one of the most remarkable properties of its salts, namely, that the halogens and acid radicles which they may contain are not removable with equal facility. Thus, for example, the four chlorine atoms in Gros's

chloride are not equally precipitable by silver nitrate, a fact which may be explained by saying that it contains two chlorine ions and two undissociated chlorine atoms. One of the sulphates prepared by Cleve had the same empirical composition as a basic sulphate derived from Gros's base, but only one of the three equivalents of sulphuric acid was precipitable by barium salts. From this salt he prepared a platinum base, which he termed *Sulphatodiplatinammin*, and to which he subsequently gave the formula



Some of the early work on the platinum bases, more particularly that on Gros's compounds, was done in Würtz's laboratory in Paris, but in 1868 Cleve returned to Sweden and worked for some months in the mineralogical laboratory of the Stockholm Academy of Sciences. Here he discovered an entirely new series of these complicated compounds, which he obtained by the action of ammonia on the iodine derivatives of Gros's base. They were the first representatives of these bases containing the double platinum atoms, and were termed by him the diplatinammin compounds. He eventually gave to them the following rational formula:—



In his attempt to gain a true conception of the constitution of the metal-ammonia bases Cleve undoubtedly obtained great assistance from Blomstrand, and there is no question that the "Chemie der Jetztzeit," which was published in Heidelberg in 1869, and in which Blomstrand developed and extended his views of the mutual relations of these various groups of substances into an orderly and systematic arrangement, gave Cleve his first clear insight into their constitution and interdependence. The effect on him was immediate, and is to be seen in his next memoir in 1870 on the isomeric platinum bases, in which he finally renounces the Berzelian system of representation and notation in favour of the more comprehensive and rational scheme, founded on valency, which still satisfies us.

In this paper he describes a number of derivatives of Reiset's second base, as well as a series of salts isomeric with these. The first members of these latter salts were discovered by Peyrone, but their true relations remained hitherto obscure. These compounds were termed by Cleve the platinoxydulammonium salts. His

study of the properties of the two isomeric series led him to suggest the following formulæ as expressing their constitution:—

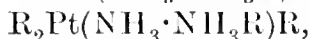


Chloride of Reiset's second base.



Platinoxydammmonium chloride.

Cleve further found that tetravalent platinum gave rise to a series of salts, obtained from platinoxydammmonium, isomeric with Gerhardt's platinammine compounds. The two series of compounds discovered by Cleve, $\text{Pt}(\text{NH}_3 \cdot \text{NH}_3\text{R})\text{R}$ and



were subsequently termed by Blomstrand, whose classification and nomenclature of the platinammonium compounds is still commonly adopted, the platosemiammines and platinsemiammines, whereas the isomeric bases of Reiset, $\text{Pt}(\text{NH}_3\text{R})_2$, and Gerhardt, $\text{R}_2\text{Pt}(\text{NH}_3\text{R})_2$, were styled respectively platosammines and platinammines.

In order to obtain further experimental support for his views of the constitution of these isomerides, Cleve studied their behaviour towards aniline. He found that in the case of the compound obtained from the platosammine chloride the two aniline molecules were readily split off, whereas in that derived from the platosemiammine chloride a molecule of aniline remained. In the first case we had



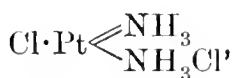
whilst in the second we had, according to Cleve,



Cleve's view that both classes of salts contain divalent platinum is, however, hardly probable in view of Jörgensen's later work. The constitution of the corresponding chlorides would seem, on the whole, to be better represented by the formulæ

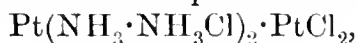


and

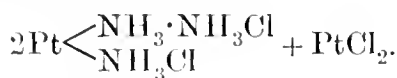


although Cleve's expression has the merit of clearly indicating the important fact of the different behaviour of the chlorine in the two isomeric chlorides.

This paper was followed (1871) by a short communication in which Cleve explained the relation between the green salt of Magnus, platodiammine chloride platinous chloride,



and the brown salt discovered by Peyrone—the first member of the platosamminesemidiammine series—



The chloride $\text{Pt} \begin{array}{c} \text{NH}_3\text{NH}_3\text{Cl} \\ \text{NH}_3\text{Cl} \end{array}$ may be caused to combine with two

atoms of chlorine, when it forms $\text{Pt} \begin{array}{c} \text{Cl} \\ \text{NH}_3\text{NH}_3\text{Cl} \\ \text{NH}_3\text{Cl} \\ \text{Cl} \end{array}$.

The corresponding platinamminesemidiammine derivatives were also prepared by Cleve.

In the same year he published two papers on the sulphites and nitrites of the isomeric bases of platosammine and platosemidiammine.

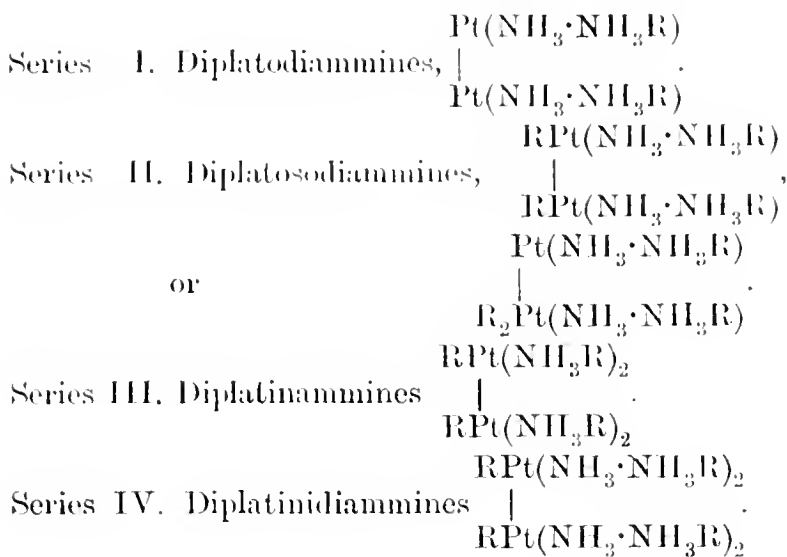
The work on the ammoniacal platinum bases occupied Cleve nearly six years, and he put together his results in a remarkable memoir, written in English and published by the Swedish Academy of Sciences in 1872, a copy of which is to be found in our Library. In this memoir, which extends to upwards of 100 4to. pages, Cleve arranges all the known derivatives of the ammoniacal platinum bases in accordance with Blomstrand's scheme of classification, using his system of terminology. The whole of these bodies—many hundreds in number—may be grouped under three main divisions, each division being subdivided into several series, as follows:—

Group I.—*Plato- or Platoso-compounds.*

- Series I. Platosemiammines, RPtNH_3R .
 „ II. Platosammines, $\text{Pt}(\text{NH}_3\text{R})_2$.
 „ III. Platodiammines, $\text{Pt}(\text{NH}_3\text{NH}_3\text{R})_2$.
 „ IV. Platosemidiammines, $\text{Pt}(\text{NH}_3 \cdot \text{NH}_3 \cdot \text{R})\text{R}$.
 „ V. Platomonodiammines, $\text{Pt}(\text{NH}_3 \cdot \text{NH}_3\text{R})(\text{NH}_2\text{R})$.

Group II.—*Platini- or Platin-compounds.*

- Series I. Platinammines, $\text{R}_2\text{Pt}(\text{NH}_3\text{R})_2$.
 „ II. Platinidiammines, $\text{R}_2\text{Pt}(\text{NH}_3 \cdot \text{NH}_3\text{R})_2$.
 „ III. Platinisemidiammines, $\text{R}_2\text{Pt}(\text{NH}_3 \cdot \text{NH}_3\text{R})\text{R}$.
 „ IV. Platinimonodiammines, $\text{R}_2\text{Pt}(\text{NH}_3 \cdot \text{NH}_3)\text{R}(\text{NH}_3\text{R})$.
 „ V. Platinitriammines, $\text{R}_2\text{Pt}(\text{NH}_3 \cdot \text{NH}_3 \cdot \text{NH}_3\text{R})_2$.

Group III.—*Diplatinum Compounds.*

Although Cleve entitles his memoir “On Ammoniacal Platinum Bases,” its subject-matter really comprehends the discussion and systematic arrangement of all the metalline ammoniacal bases and their salts at that time known, and must have involved great labour and research in its compilation.

From this review of all the known ammoniacal compounds of the different metals Cleve concluded:—

I. The highest number of molecules of ammonia which occur united together in ammoniacal compounds is 4. *Tetrammines* of calcium, strontium, and perhaps of cuprosum are as yet the only ones known.

II. *Triammines* are formed by calcium, magnesium, cobalt, nickel, zinc, cadmium, silver, rhodium and iridium.

III. *Diammines* are produced by most metals.

IV. Consequently, as a rule, the most positive metals seem to have the power of uniting the greatest number of molecules of ammonia, but more negative metals, such as platinum, form the most stable ammoniacal compounds.*

During some portion of the time over which this work extended, Cleve found opportunity to gratify his inclination towards the study of natural history. Shortly after his return from Paris he

* The prefixes *mono-*, *di-*, &c., denote the number of NH_3 groups directly united with one another, and not the number of such groups in direct union with the Pt atom. Thus, as the compounds in Series III, Group II, contain $(\text{NH}_3 \cdot \text{NH}_3)$ or one diammine chain, they are called *semi-diammines*; and as those in Series IV, Group II, contain one diammine and one monoammine chain, they are termed *mono-diammines*.

was enabled, by means of a grant from the Stockholm Academy of Sciences, to undertake a journey to the West Indies with a view to an inquiry into the geological structure of the Antilles, the results of which were published in 1871 in English, by the Swedish Academy.

On his return he was made Adjunct in Chemistry in what was then known as the Stockholm Technological Institute, but which has now developed into a polytechnic of the type of Charlottenburg or Zurich. Whilst occupying this position he did a considerable amount of literary work, compiling text-books and putting together many contributions to the periodical literature of the time on botanical and geological subjects. On Svanberg's retirement he was called to the Chair of Chemistry in Upsala, where he remained until the age-limit of sixty-five which operates in Sweden required him to resign the Professorship.

Shortly before his removal from the Swedish capital to Upsala, Cleve turned his attention to the study of the rare earths—a branch of chemical inquiry with which the names of Scandinavian investigators are pre-eminently associated. As is well known, Sweden has the good fortune to possess an uncommon share of those minerals which are characterised by containing the so-called rare earths—one small locality alone, namely, Ytterby, not far from Stockholm, was famous as the happy hunting-ground of the collector—and the investigation of this material was long the monopoly of Swedish chemists, as the names of Gadolin, Ekeberg, Mosander, Berzelius, Hisinger, and Bahr testify. The greater part of their work in this special department of mineral chemistry was done during the first third of the nineteenth century, and resulted in the addition of no fewer than seven substances to the list of the chemical elements then known, namely, yttrium, cerium, thorium, lanthanum, didymium, terbium, and erbium. The death of Berzelius and the consequent disappearance of his school, together with the extraordinary development of organic chemistry, due mainly to Liebig and his associates in Germany, and to Dumas, Laurent and Gerhardt, and others in France, undoubtedly checked the progress of inquiry in the special field which the Swedish chemists had cultivated with such brilliant success. But the discovery of the remarkable absorption spectrum of didymium by Gladstone, and of that of erbium by Bahr, led to renewed activity in rare-earth chemistry, and the services of the spectroscope as an analytical instrument were at once brought into requisition in connection with this department of inorganic chemistry.

It was at this juncture that Cleve and his collaborator Höglund entered the field, and in a paper published in 1872 they gave the

results of an inquiry which covered much the same ground as a prior investigation by Bahr and Bunsen on the gadolinite earths.

Incidentally, however, Cleve and Högblund prepared a large number of hitherto undescribed salts of yttrium and erbium, both of which they regarded at that time as divalent elements.

The publication by Mendeléeff of the epoch-making memoir in which he first made known the great generalisation which is associated with his name resulted in further attention being paid to the chemistry of the rare earths. As will be remembered, Mendeléeff in this paper discussed the position of certain of the rare-earth metals in the periodic system, and showed that all the known facts rendered it in the highest degree probable that the greater number of these elements must be regarded as belonging to the third group of his scheme of classification. Cleve at once recognised that the systematic study of this group of elements in the light of Mendeléeff's generalisation would constitute one of the strongest tests of its validity. He repeated and extended his work with Högblund on the compounds of yttrium and erbium, and then attacked the chemistry of the elements thorium, lanthanum, and didymium. No stronger evidence of Cleve's power of work could be adduced than is shown in the monograph published in 1874, embodying the results of the two years' labour, on the compounds of these five metals. Concurrently with this inquiry, Jolin, under Cleve's direction, took up the study of the salts of cerium. As the result of this comprehensive investigation, Cleve established that thorium is certainly a quadrivalent element, whilst the other metals constitute a natural group of chemically related bodies, of which cerium and lanthanum, on the one hand, and yttrium and erbium on the other, form subgroups, the respective members of which stand in close relationship to each other, their compounds, as Marignac and Topsoë had shown, being respectively isomorphous; whereas didymium would appear to occupy an intermediate position, as it forms salts which are isomorphous sometimes with the one subgroup and sometimes with the other. If we assume with Cleve that lanthanum is to be regarded as trivalent, it follows that the remaining four elements are also trivalent, a conclusion which Cleve sought to establish by the preparation of a large number of typical salts. Cleve's main conclusions were not universally accepted at the time of their publication, and indeed were freely criticised by Delafontaine and by Wyrouboff, but all subsequent inquiry has served to establish their validity, and the position of these elements in the schemes of classification at present in vogue is practically that which Cleve indicated.

Some years later, and mainly in consequence of the work of

Frerichs and Smith, Cleve was induced to repeat certain of his observations on the compounds of lanthanum and didymium. He confirmed his results, with, however, this significant difference, that for the first time he was led to give expression to his doubt as to the individuality of didymium. He founded this surmise mainly on the behaviour of didymium oxide on heating, the change in colour suggesting the presence of another element.

How well founded was this surmise was established by Auer von Welsbach in 1885 by the discovery of praseodymium.

In the years immediately following the publication of Cleve's papers, the chemistry of the rare-earth metals received important extensions by the discovery of ytterbium by Marignac and of scandium by Nilson. Shortly after the existence of the latter element was made known, Cleve was enabled to prepare a number of its salts, and to make the first determinations of its atomic weight, with the result of proving that scandium was identical with Mendeléeff's ekaboron. It is hardly necessary to remind you of the effect on the chemical world of this discovery. It was the second instance of the realisation of Mendeléeff's prediction as to the existence of hitherto unknown elements the properties of which he had been able to forecast by the aid of the principles he first clearly indicated. The realisation of these predictions, coming so soon after the promulgation of the Periodic Law, did more to secure its general acceptance among men of science than any other set of facts.

Marignac's discovery of ytterbium in what was generally regarded as a homogeneous earth rendered it almost certain that the properties up to that time associated with erbia were not those of an individual substance, and accordingly Cleve set himself to prepare pure erbia with a view to an accurate study of its characters and a redetermination of its atomic weight. No erbia that Cleve could at the outset obtain furnished constant atomic weight values, and he concluded, therefore, that Mosander's erbia was even a more complicated mixture than had hitherto been surmised. Thalén's investigation of the spectroscopic behaviour of the several fractions obtained by Cleve showed that they contained, in addition, possibly, to other substances, at least two new elements, one having an atomic weight between that of erbium and of yttrium—that is between 166 and 89, and the other having an atomic weight between those of erbium and ytterbium—that is between 166 and 173. The former Cleve named *holmium*, the latter he called *thulium*. Holmium appears from its spectroscopic indications to be identical with Soret's X. It is still doubtful, however, whether holmia and thulia are actually simple substances; there is good reason to believe, indeed, that Cleve's holmia is in reality a mixture containing possibly unknown elements.

Unfortunately, these substances are present in the gadolinite earths in extremely small quantity, and their separation is both tedious and imperfect.

Although Cleve was unable to do more than indicate the probable existence of these new elements in gadolinite, he eventually succeeded in obtaining pure erbia, and the atomic weight which we now associate with that element is based upon his determinations.

The discoveries made subsequent to 1874 led Cleve to undertake a revision of his determinations of the atomic weights of yttrium, lanthanum and didymium. As regards yttrium and lanthanum, the repetition resulted in comparatively unimportant changes; in the case of didymium the number was much too high, owing to the presence of samarium, prior to that time unknown. The number obtained by Cleve on repetition was 142, almost the arithmetic mean of the atomic weights of its two subsequently discovered components, praseodymium, 140.5, and neodymium, 143.6.

Cleve next studied the action of hydrogen dioxide upon the rare earths, and described a number of their peroxides, and in 1883 and 1885 he published important papers on samarium and its salts, and gave the first accurate estimation of its atomic weight.

These constituted his last contributions to this department of mineral chemistry, although he continued to the end to take an interest in its further development, placing the stores of material which he had accumulated in the Upsala laboratory at the disposal of such of his students as were willing to devote themselves to its investigation, and who were, at the same time, capable of taking advantage of the advice and counsel which his own ripe experience enabled him to give. It is only necessary to name the monographs on praseodymium by Schéele, on ytterbium by Astrid Cleve, on gadolinium by Benedicks, and on neodymium by Holmberg, to show that these treasures have been turned to good account.

As is well known to all here, the rare earths have acquired an increased importance within recent times owing to their technical value in connection with artificial illumination, and the whole world is now being searched for new sources of supply. Even now undreamt-of amounts of certain of them resulting from the operations needed to extract the commercially valuable oxides are at the disposal of investigators, and we may confidently anticipate, therefore, fresh additions to knowledge in a field of inquiry where much still remains to be done.

Cleve's services to inorganic chemistry, and especially to rare-earth chemistry, were recognised by the Royal Society in 1894 by the award to him of the Davy Medal. In presenting the medal, the President, Lord Kelvin, said: "This field of inquiry is pre-eminently Scandinavian. By the manner in which he has cultivated

it, Professor Cleve has shown himself a worthy successor of such forerunners as Gadolin, Berzelius and Mosander, and by sound and patient investigation he has faithfully upheld the traditions inseparably associated with these names. All chemists are agreed that no department of their science demands greater insight or more analytical skill than this particular section. Many of the minerals which furnish the starting point for investigation are extremely rare, and the amounts of the several earths which they contain are frequently very small. Moreover, the substances themselves are most difficult of isolation, and their characters are so nearly allied that the greatest care and judgment are required in order to determine their individuality. A remarkable example of Professor Cleve's power in overcoming these difficulties is seen in his masterly inquiry into the affinities and relations of the element scandium, discovered by Nilson. This, one of the rarest of the metals, is found only in gadolinite to the extent of 0.003 per cent.; and in yttritanite to the extent of about 0.005 per cent. The whole amount of the material, as oxide, at Cleve's disposal was only about 1 gram, but with this small quantity he determined the atomic weight of the element, and ascertained the characters of its salts with such precision as to leave no doubt of the identity of scandium with the element *Ekabor*, the existence of which was predicted by Mendeléeff, in the memorable paper in which he first enunciated the Law of Periodicity. Cleve's research, indeed, constitutes one of the most brilliant proofs of the soundness of the great generalisation which science owes to the Russian chemist.

A not less remarkable instance of Cleve's skill as a worker is seen in his research on samarium and its compounds, which he communicated, as one of its Honorary Foreign Fellows, to the Chemical Society of London. The existence of samarium was inferred independently by Delafontaine and Lecoq de Boisbaudran, but we owe to Cleve the first comprehensive investigation of its characters and chemical relations. From the nature of its compounds, a large number of which were first prepared and quantitatively analysed by Cleve, and from the value of its atomic weight, which was first definitely established by him, it would appear that samarium most probably fills a gap in the eighth group of Mendeléeff's system."

And perhaps I may be pardoned for saying that there is no circumstance in my official connection with the Royal Society which I have greater pleasure in recalling than the share I was permitted to take, as a member of its Council, in thus testifying to the appreciation which all British chemists feel of the value of Cleve's services to their science.

Cleve's name is associated with descriptive mineralogy in con-

nection with a mineral first made known by Nordenskjöld in 1878, and which is of importance from its relation to the history of argon and helium. It will be remembered that Hillebrand, in 1890, announced that gaseous nitrogen was a constituent of cleveite. Shortly after the discovery of argon, Cleve directed his pupil Langlet to make a further investigation of the gases in this mineral. The results of this inquiry were, however, anticipated by Ramsay, who discovered that the characteristic gases of cleveite were helium and argon. Langlet made use of the helium thus extracted to make the first accurate determinations of its atomic weight, and obtained the value $\text{He}=4.0$ which finds its place in our tables.

As director of the Upsala laboratory, then, as now, the most important school of chemistry in Sweden, Cleve was anxious to secure for organic chemistry its proper position in the scheme of instruction in the University. Since the death of Berzelius, Sweden had mainly won her laurels in the fields of mineral chemistry, but no teacher in Cleve's position could be unmindful of the extraordinary development of the chemistry of the carbon compounds which had resulted from the activity of French and German workers, or oblivious of the material benefits which followed from the technical applications of their discoveries.

It was incumbent on him, therefore, to arrange that Upsala should take her due share in the cultivation of this great and rapidly extending branch of inquiry. Although it might be expected that Cleve's predilections as a worker would be to continue in the line of investigation with which he had been associated for so many years past, and in connection with which he had accumulated such rich stores of material, he determined to embark himself upon the great ocean of organic research with such of his pupils as were disposed to accompany him. As might have been surmised, he was mainly attracted by problems of isomerism and constitution, and he found in the chemistry of naphthalene ample scope for the exercise of his powers. Cleve began by attacking the constitution of the nitrosulphonic acids. This he and Atterberg sought to unravel by converting them into the corresponding dichloronaphthalenes by the methods of Carius, Koninck and Marquardt. This field of inquiry occupied the Upsala laboratory for about eighteen years. When Cleve entered it only two of the ten possible dichloronaphthalenes were known. He himself prepared six of the isomerides, and Atterberg obtained two more in addition. Only those who have occupied themselves with work of this character can fully realise how tedious and time-consuming it is owing to the very slight differences in physical characters which certain of the substances possess.

The nitrosulphonic acids prepared by Cleve of which he was able to determine the constitution were the 1·5, the 1·6, 1·3, 1·7, 1·8 and 1·4. He also prepared the corresponding amino-acids, of which the 1·6 and 1·7 are of special importance in the colour industry, and are known in technology as Cleve's naphthylaminesulpho-acids.

Cleve and his pupil Arnell also prepared and studied eight of the fourteen possible chloronaphthalenesulphonic acids, namely, the 1·4, 2·6, 2·8, 1·5, 1·6, 1·3, 1·2 and 1·7 isomerides, and he further prepared many of the nitro-compounds, the constitution of which he determined by conversion into the trichloronaphthalenes. Other coadjutors in this work in the Upsala laboratory were Jolin, Widman, Ekstrand, Forsling and Ekbom.

In awarding the Davy Medal Lord Kelvin also made allusion to the naphthalene work, and to the manner in which Cleve had thus gradually brought order out of confusion, adding that: "Within recent years a score of workers have occupied themselves with the same field of research, and no greater proof of Cleve's accuracy and care as an investigator could be furnished than the manner in which his naphthalene work—confessedly one of the most intricate and complicated sections of the chemistry of aromatic compounds—has stood the ordeal of revision."

No account of the outcome of the Upsala laboratory whilst under Cleve's direction would be complete without some allusion to the fact that it was during that period and in that place that Svante Arrhenius acquired his knowledge of chemical science. The celebrated memoir of 1884 in which Arrhenius first promulgated the theory which has made him famous was his Doctor-Dissertation at Upsala.

Cleve, who, I have good grounds for stating, greatly appreciated his honorary membership of our Society, published several of his contributions to the literature of chemistry in our Journals. Among these was his first memoir on samarium, which appeared in our Transactions in 1883. He also published a short note in our Proceedings, in 1891, on the formation of an explosive substance from ether. Lastly I may remind you of the obligation which the Society is under to him for the admirable critical estimate of the life-work of his friend Marignac which forms the memorial lecture on our distinguished Foreign Member.

Although Cleve continued to the end of his academic career to interest himself in the proper work of his chair, reading the periodical literature of our science with regularity, and studying to keep himself informed of its development, towards the close of his life he became more and more absorbed in those biological studies to which he had never ceased to be attracted, and latterly

he gave himself entirely to them. Of his work on the diatoms and on plankton—most of which was published in English—this is not the place to speak, even if I were competent to offer any opinion concerning it. That it should have secured for him the honorary membership of the Royal Microscopical Society—a distinction which he prized not less than his fellowship in our Society—is some evidence of the value which contemporary workers set upon his labours.

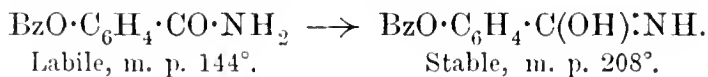
When the time for his retirement from the Chair at Upsala arrived, he moved to Gothenburg that he might be near the sea and in touch with the hydrographic station at Bornö, and thus pursue uninterruptedly and in quietude the study of his beloved plankton. Of a sound constitution and of good bodily strength, regular and methodical in his habits, active in mind, serene in temper, and unimpaired in intellectual vigour, he might still at sixty-five look forward to many years of scientific activity. But these years were not to be his. In December of 1904 he was suddenly seized with pleurisy. His heart became affected, and cardiac asthma supervened. In the spring of 1905 he was somewhat better and journeyed to Upsala, but died there, within three weeks of his arrival, on the 18th of June, 1905.

His memory will be cherished by those who had the privilege of his friendship as that of a true man, vigorous in intellect, rich in mental acquirement, wide in sympathy with every branch of natural science, courteous in manner, calm and unimpassioned in judgment, of a humour ironical at times and even mordant, but withal tolerant and large-hearted, and of a flexibility of opinion, especially on theoretical questions, which was often disconcerting to his friends. And in the annals of science his name will continue to live as that of one who followed her unselfishly and gave unstintedly to her service all that was best in him.

CXXXII.—*Labile Isomerism among Acyl Derivatives of Salicylamide.*

By JAMES McCONNAN and ARTHUR WALSH TITHERLEY.

THE benzoylation of salicylamide, as was shown by one of the authors (Trans., 1905, 87, 1207), may give rise to two mono-benzoyl derivatives. One of these, *O*-benzoylsalicylamide (m. p. 144°), $\text{BzO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$, is labile and readily passes into the other, a stable compound melting at 208° and identical with the product obtained by Gerhardt and Chiozza (*Ann. Chim. Phys.*, 1856, 46, 169; *Jahresber.*, 1856, 502) by heating benzoyl chloride and salicylamide. Owing to the anomalous properties of this compound there is some doubt as to its constitution. Titherley and Hicks (Trans., 1905, 87, 1207) showed that its properties were not consistent with the expected *N*-benzoyl formula, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{Bz}$, but adduced evidence showing that the benzoyl group was attached to the phenolic oxygen atom, and concluded that it was probably an iminohydroxide and not a true amide, the relation between the two benzoyl derivatives being represented thus:

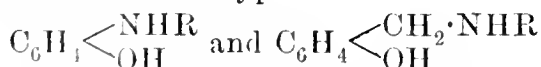


Auwers (*Ber.*, 1905, 38, 3256) objected to this hypothesis and regarded Gerhardt's benzoylsalicylamide (m. p. 208°) as the simple *N*-benzoyl derivative, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHBz}$, and this view was also held, chiefly on the evidence of a faint ferric chloride reaction, by Einhorn and Schupp (*Ber.*, 1905, 38, 2793). In a later paper, Einhorn and Haas (*Ber.*, 1905, 38, 3627), in discussing the instability of salicylamide carbonate, $\text{CO} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$, which should be formed by the action of concentrated sulphuric acid on the nitrile,



but which decomposes into salicylamide and carbonylsalicylamide,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C}=\text{O} \end{smallmatrix}$, regard this rearrangement as further evidence in support of Auwers' view that Gerhardt's compound is an *N*-benzoyl derivative. Auwers' theory as to the isomeric change observed by Titherley and Hicks involves the transport of a benzoyl group, and in support of this view he quotes his work on the acylation of ortho-hydroxy-aromatic amines of the type



(*Annalen*, 1904, 332, 159), in which he has shown that the *O*-acyl

derivatives, owing to their instability, immediately pass into the *N*-acyl isomerides.

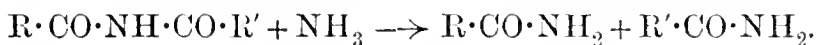
As, however, the properties of Gerhardt's compound do not entirely support this theory, the authors have further investigated the substance, as well as a series of other acyl derivatives of salicylamide, in the hope of throwing light on what promised to be an interesting problem. The result has been to show that the simple *N*-benzoyl formula cannot be accepted and that acyl salicylamides in general exhibit remarkable labile isomerism. It has been clearly demonstrated that Gerhardt's benzoylsalicylamide is tautomeric and can behave as if the benzoyl were attached to both *N* and *O*; but it has been further made clear that the iminohydroxide formula of Titherley and Hicks is no longer tenable. The following *résumé* of the more characteristic properties of this substance illustrates its tautomeric character.

(1) *Properties supporting the N-Benzoyl Formula*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHBz} \\ \text{OH} \end{smallmatrix}$.

—Gerhardt's compound is soluble in sodium or ammonium hydroxides and forms a silver salt. The latter with methyl iodide yields a methyl derivative which has been identified as $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHBz} \\ \text{OMe} \end{smallmatrix}$, since the same compound (m. p. 141°) has been synthesised by the pyridine-benzoylation of *O*-methylsalicylamide. With diazomethane, Gerhardt's compound reacts in ethereal solution yielding the same *O*-methyl-*N*-benzoyl salicylamide. With alcoholic ferric chloride it gives a red coloration so faint as to have been overlooked by Titherley and Hicks.

(2) *Properties opposed to the N-Benzoyl Formula*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHBz} \\ \text{OH} \end{smallmatrix}$.—

It is not affected, as was shown previously, by warming with aqueous ammonia. The authors have shown that secondary amides are readily decomposed by this treatment, giving primary amides,* thus :



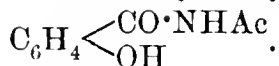
Anwers (*Ber.*, 1905, 38, 3256) explains the stability of the compound towards ammonia by assuming that the OH-group exerts an inhibiting influence: (1) owing to its ortho-position and (2) by leading to salt formation similar to that which E. Fischer (*Ber.*, 1898, 31, 3274) has shown hinders the hydrolysis of certain esters and amides by sodium hydroxide. Although this argument may be sound, its insufficiency in reference to (1) is demonstrated by the now well-established fact that both $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHBz} \\ \text{OBz} \end{smallmatrix}$ and $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHAc} \\ \text{OBz} \end{smallmatrix}$, isolated by Titherley and Hicks, which contain heavier ortho-groups, are rapidly decomposed

* This interesting reaction of secondary amides is under investigation, the results of which will be communicated later.

by ammonia, yielding the same compound (Gerhardt's benzoylsalicylamide), whilst $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NBz}_2 \\ \text{OBz} \end{smallmatrix}$ is not affected by ammonia. In reference to (2), Fischer did not show that salt formation completely prevents hydrolysis. Heated in a sealed tube with ammonia, Gerhardt's compound yields salicylamide and benzoic acid, a reaction which is inconsistent with the *N*-benzoyl formula. With phosphorus oxychloride, it yields benzoylsalicylnitrile, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CN} \\ \text{OBz} \end{smallmatrix}$ (m. p. 105°), as has been shown by one of the authors (Proc., 1905, 21, 288).

On boiling with acetic anhydride it yields *O*-benzoyl-*N*-acetylsalicylamide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHAc} \\ \text{OBz} \end{smallmatrix}$ (see p. 1324), and on pyridine benzoylation at -15° it yields a mixture of two benzoyl derivatives (see p. 1326).

Perhaps, however, the most convincing evidence against the simple *N*-benzoyl formula for this substance is to be found in a comparison of its properties with those of *N*-acetylsalicylamide,

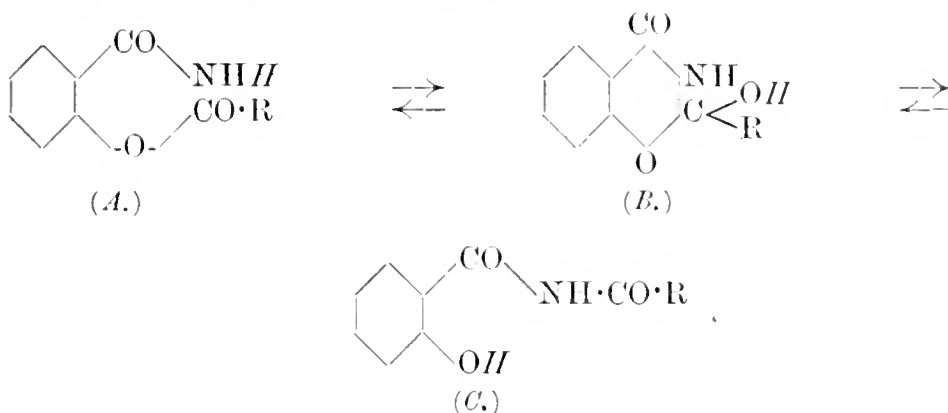


The latter, which has been isolated by the authors, exhibits quite normal properties; it gives an intense reddish-violet ferric chloride reaction; it gives only a faint yellow colour with ammonia, by which it is rapidly decomposed; and, unlike Gerhardt's compound, it possesses the usual solubility relations of secondary amides. Moreover, in accordance with its true phenolic character, it gives an abnormal molecular weight by the cryoscopic method, whilst Gerhardt's compound gives a normal result.

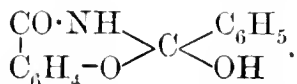
Statement of Hypothesis.—To account for the conflicting evidence as to the constitution of Gerhardt's benzoylsalicylamide and to explain the peculiar relations observed among the acyl salicylamides, various hypotheses have been considered; of these, the only one which is consistent throughout is that of cyclic tautomerism, in which the alternative tautomeric forms are an open chain and a ring. Gerhardt's compound by this hypothesis may be represented as the ring derivative, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{OH} \end{smallmatrix}$, and this formula was tentatively suggested by Titherley and Hicks (*loc. cit.*, p. 1211), but rejected for want of evidence. With a mass of accumulated observations now in hand, the ring hypothesis has been adopted, since it furnishes a satisfactory explanation of the apparently contradictory features of this investigation.

Assuming in the labile *O*-acyl salicylamides that the CO of the acyl group engages with the hydrogen of the CO·NH₂ group in close proximity, forming a cyclic hydroxy-derivative which may be

tautomeric, a compound results which, if stable, remains as such (*B*), or, if unstable, may undergo one of two changes: (1) the hydroxyl *H* may wander back to the nitrogen atom (giving *A*), or (2) may wander to the phenolic oxygen atom (giving rise to *C*). With a perfectly reversible system the scheme is thus:



Varying grades of stability of the types *A*, *B*, and *C* might be expected according to the nature of *R*, and according to whether the residual hydrogen of the *NH* group is further substituted. Taking the mono-benzoylsalicylamides as concrete examples, form *A* exists as a labile compound, $\text{Bz} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ (m. p. 144°), which, stable at 15° , passes on heating or in ionising solvents extremely easily into *B* or *C*, forming the stable derivative (Gerhardt's compound, m. p. 208°), which is tautomeric and may equally well possess the open chain, $\text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, or closed chain formula,



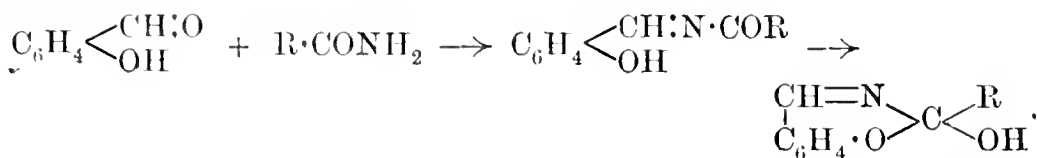
Only on this assumption can its peculiar behaviour be satisfactorily accounted for. Conversely, all attempts to prepare *N*-benzoylsalicylamide by the recognised methods of amide acylation (Titherley, *Trans.*, 1904, 85, 1673) lead to the production of Gerhardt's compound ($B \rightleftharpoons C$). Lastly, the authors have shown that this compound is stable only in a relative sense, and on heating with glacial acetic acid may be converted largely into the so-called labile *O*-benzoylsalicylamide (*A*). This change is difficult to reconcile with Auwers' hypothesis, which assumes a simple wandering of the benzoyl group from *O* to *N*.

It is evident that such a scheme of reversible change, involving ring production in one of the tautomeric forms, is analogous to the so-called lactone tautomerism which is shown by certain di-aldehydes (for example, succinaldehyde and phthalaldehyde) or γ -aldehydic and γ -ketonic acids; and the analogy is sufficiently complete, implying the engagement between a *CO* group and a mobile hydrogen atom, to render the change a likely one. The ring form contains the metox-

azine skeleton  as a derivative of benzometoxazone, and on

this account the authors propose to name this new kind of change "metoxazone tautomerism."

A rearrangement somewhat analogous to this has already been observed by Cebrian (*Ber.*, 1898, **31**, 1592), who, in condensing salicylaldehyde with primary amides in presence of sodium acetate, obtained products which were evidently cyclic, and which he named "cumarazines," thus:



Cebrian's cumarazines, which are apparently stable, contain the same metoxazine skeleton as the cyclic tautomeric forms of the authors' acyl salicylamides (phenylhydroxybenzometoxazones).

If the simple theory of acyl-wandering, by which Auwers explains the conversion of the labile benzoylsalicylamide into its stable isomeride, be accepted, it would be necessary to assume, in the acyl salicylamides now known, an unprecedented mobility of acyl groups, as will be shown; whilst a cyclic mechanism avoids this difficulty, and also explains why the labile phenomena are restricted to acyl derivatives of salicylamide, the alkyl derivatives of the latter showing no such tendency to change.

The following brief statements of the relationships observed in the present investigation will serve to illustrate the perplexing nature of the problem and support the theory as to metoxazone tautomerism.

O-Acetylsalicylamide, $\text{AcO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ (m. p. 138°), is obtained by the pyridine-acetylation of salicylamide at -15° , and its structure follows from its chemical properties as well as from the fact that it may also be synthesised by the action of ammonia gas on *O*-acetyl salicyl chloride, $\text{AcO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{Cl}$. On treatment with aqueous ammonia, or on heating or standing in pyridine solution at 15° , it is readily transformed into an isomeride melting at 147° , a change analogous to the rearrangement of *O*-benzoylsalicylamide; but the isomeride has markedly different properties from Gerhardt's compound, and behaves as the true *N*-acetylsalicylamide, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHAc}$.

It is evident that the ring formula $\begin{array}{c} \text{CO} \cdot \text{NH} \\ | \quad \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 - \text{O} \quad \text{C} \begin{array}{c} \text{C}_6\text{H}_5 \\ \diagdown \\ \text{OH} \end{array} \end{array}$ is more stable than $\begin{array}{c} \text{CO} \cdot \text{NH} \\ | \quad \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 - \text{O} \quad \text{C} \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{OH} \end{array} \end{array}$, which apparently immediately changes to

N-acetylsalicylamide. The latter compound (not *O*-acetylsalicylamide) is also obtained by the direct action of acetyl chloride on salicylamide (through an intermediate chloro-derivative, which is subsequently decomposed by water). This method of formation, involving rearrangement, is parallel to Gerhardt and Chiozza's synthesis (*loc. cit.*) of the stable benzoylsalicylamide.

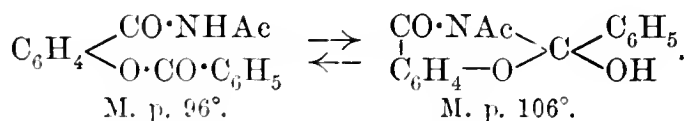
When *N*-acetylsalicylamide is benzoylated at low temperatures by benzoic anhydride or benzoyl chloride in pyridine, it gives with extreme ease an exceedingly labile derivative, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NHAc} \\ \text{OBz} \end{smallmatrix}$ (m. p. 95°), originally obtained by Titherley and Hicks (*loc. cit.*) from *O*-benzoylsalicylamide, and the same compound is produced with difficulty by the pyridine benzoylation of *O*-acetylsalicylamide (evidently rearranged before benzoylation). The difference in the ease of benzoylation is in conformity with the above deductions as to the constitution of the two acetylsalicylamides.

The constitution of the labile compound melting at 96° follows from the above easy synthesis, and is confirmed by a method involving treatment with cold concentrated sulphuric acid and exposure to atmospheric moisture. This process differentiates between *O*-acyl and *N*-acyl derivatives, inasmuch as the former are completely hydrolysed and the latter not affected; and it has been shown, for instance, that whilst phenyl benzoate or acetate or salol are in this way hydrolysed, dibenzamide and acetylbenzamide are not. The method has been extensively used by the authors as a means of locating an acyl group. As the compound m. p. 96° on this treatment yields only *N*-acetylsalicylamide m. p. 147° , its constitution as *O*-benzoyl-*N*-acetylsalicylamide follows. When this compound is heated, it is converted into a somewhat more stable isomeride melting at 106° , and in many cases the latter accompanies the other in its synthetic production unless great care is exercised. The relations between the two isomerides are of a remarkably labile character and perfectly reversible. The isomeride m. p. 106° is completely converted into that melting at 96° by warming with acetic anhydride. Each can be crystallised unaltered from dilute solution in hot light petroleum. But if the compound of m. p. 96° is dissolved in an excess of boiling light petroleum and cooled so as to form a supersaturated solution, the isomeride of m. p. 106° separates as opaque, voluminous, warty masses on nucleating the solution with a small portion of this substance. Conversely, from a cold supersaturated solution of the compound m. p. 106° , the isomeride m. p. 96° separates as very long needles on nucleating the solution with a small quantity of the substance, provided that the supersaturation is not too great. Under less carefully regulated conditions of concentration, the compound m. p. 96°

on crystallisation from hot light petroleum may, through partial or complete rearrangement, give rise to a mixture of the two isomerides or wholly that melting at 106°.

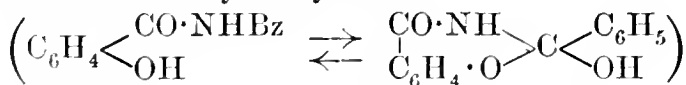
It is evident that either compound in light petroleum solution tends to change slowly towards an equilibrium mixture, from which it is possible to separate wholly one constituent or the other by nucleating a supersaturated solution of such a concentration that the crystallisation is slow enough to enable the disturbed equilibrium to adjust itself continually. That these two substances are not merely physical isomerides is rendered extremely probable by the following: (1) the persistence of each in crystallising unchanged from hot dilute light petroleum solution; (2) the capacity of both to crystallise together from the same solution and subsequently to persist unchanged in contact with the mother liquor. On the other hand, within the limits of experimental error the solubility of these two substances in light petroleum is apparently identical, and it is desirable that the relations between them should be further studied from a physico-chemical standpoint.

The chemical properties of the two isomerides, so far as has been ascertained, are identical. Both yield *N*-acetylsalicylamide with cold sulphuric acid, and it is quite evident that there is no exchange of acyl groups, such as Auwers' theory would necessitate, in the isomerisation. Neither compound gives a ferric chloride reaction. On the authors' hypothesis, the relation between these two isomerides is at once intelligible, the compound having the higher m. p. being the ring derivative:



Owing to the extremely easy reversibility of the isomeric change, though labile isomerides, these two substances virtually form one tautomeric substance; and had it not been for the very pronounced difference in physical appearance between them it is probable that the more unstable isomeride would have escaped observation.

When Gerhardt's benzoylsalicylamide

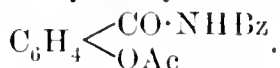


is acetylated it yields apparently contradictory results:

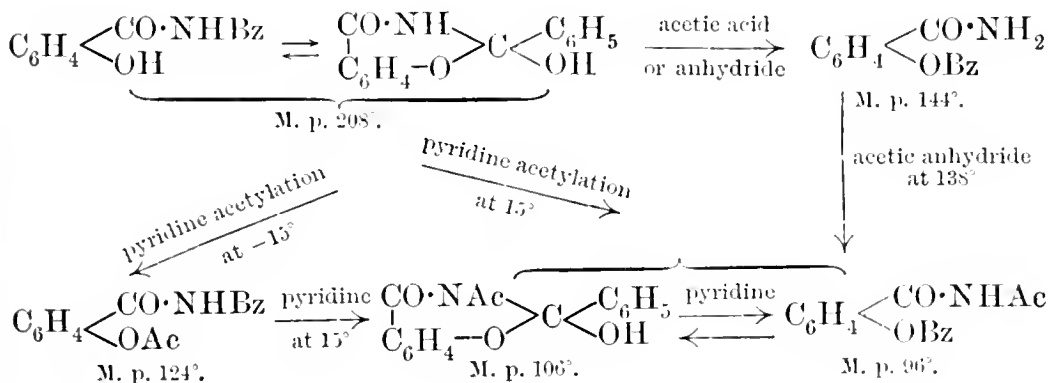
(a) Boiled with acetic anhydride it gives *O*-benzoyl-*N*-acetylsalicylamide (m. p. 96°).

(b) With acetyl chloride and pyridine at the ordinary temperature it gives a mixture of the isomerides melting at 96° and 106° respectively.

(c) With acetyl chloride or acetic anhydride and pyridine at -15° , it gives an 85 per cent. yield of an acetyl derivative, melting at 124° , which by its properties and from the fact that with concentrated sulphuric acid it gives Gerhardt's compound and acetic acid, must be regarded as *O*-acetyl-*N*-benzoylsalicylamide,

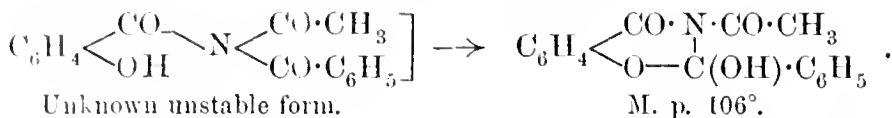
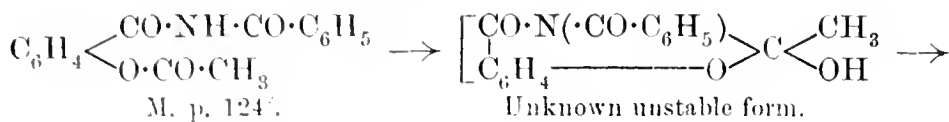


The contradiction involved in these results and the fact that no less than three acetyl derivatives may be obtained from Gerhardt's compound is in accord with its tautomeric character. In regard to (a), which at first sight appears to point to an *O*-benzoyl formula for the compound, it is clear that during heating with acetic anhydride (as with acetic acid—see before) it undergoes rearrangement to *O*-benzoylsalicylamide, which is then acetylated (as was shown by Titherley and Hicks, giving *O*-benzoyl-*N*-acetylsalicylamide, m. p. 96° ; *loc. cit.*). In regard to (b), which also appears to support an *O*-benzoyl formula for Gerhardt's compound, it has been found that *O*-acetyl-*N*-benzoyl salicylamide (the product of c) changes on standing in pyridine to a mixture of the isomerides melting at 96° and 106° ; hence the latter must be regarded as indirect (rearranged) products of acetylation. The substance obtained by method (c), *O*-acetyl-*N*-benzoyl salicylamide, must therefore be regarded as the direct product of acetylation, which thus points to the formula $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{NHBz} \\ \text{OH} \end{array}$ for Gerhardt's compound. The relations observed may be expressed in the scheme:



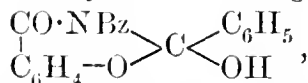
The *O*-acetyl derivative, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{C}_6\text{H}_4 \cdot \text{O} \end{array} \text{C} \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{OAc} \end{array}$, of the cyclic form of Gerhardt's compound could not be isolated.

The rearrangement of *O*-acetyl-*N*-benzoyl salicylamide (m. p. 124°) mentioned above must, on the authors' hypothesis, take place in the following manner:



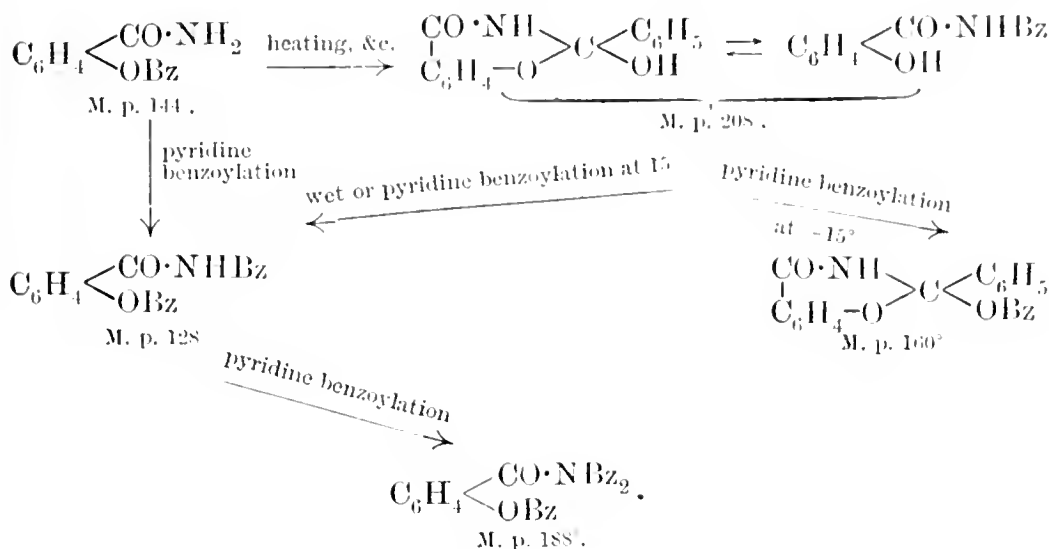
All three acetyl derivatives (m. p. respectively 96°, 106°, and 124°) are rapidly and completely decomposed by aqueous sodium or ammonium hydroxide, giving the characteristic yellow salts of Gerhardt's compound. It is obvious that the hydrolysis is accompanied by rearrangement in at least two of the compounds. The rearranging influence of alkali in this group of derivatives is very marked, and in this respect it differs from concentrated sulphuric acid, which effects preferential hydrolysis of the acyl, whether acetyl or benzoyl, attached to *O*. Alkali invariably eliminates acetyl whether attached to *O* or *N*.

The behaviour of Gerhardt's compound on benzoylation, as on acetylation, depends on conditions. On wet benzoylation or pyridine benzoylation, as was shown by Titherley and Hicks (*loc. cit.*), *O-N*-di-benzoylsalicylamide, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \cdot \text{NHBz} \\ \text{OBz} \end{array}$ (m. p. 128°), results. But by benzoylation at -15° in presence of pyridine, in addition to this compound there is formed an isomeride, m. p. 160°, which gives no ferric chloride reaction and is insoluble in caustic soda and only very slowly hydrolysed by this reagent. On the authors' hypothesis, this isomeride is the *O*-benzoyl derivative of the cyclic form of Gerhardt's compound, namely, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \cdot \text{NH} \\ \text{O} \end{array} > \text{C} \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{OBz} \end{array}$. The other possibility, that it is $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \cdot \text{NBz}_2 \\ \text{OH} \end{array}$, is inconsistent with its properties, and the only remaining possibility, that it might be

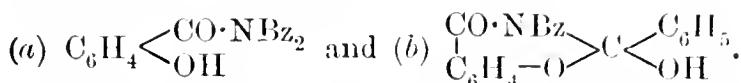


is disproved by the fact that it does not apparently allow itself to be benzoylated in presence of pyridine.

The relation between the benzoyl derivatives which have now been isolated from salicylamide as starting point are presented, according to the authors' view, in the scheme:



The scheme lacks the compounds



Attempts to prepare these compounds have failed, and it appears doubtful whether they are capable of existence in a definite stable form.

In reference to (a), *N,N*-dibenzoylsalicylamide, attempts were made to obtain it by the action of cold sulphuric acid on tribenzoyl salicylamide, thus:



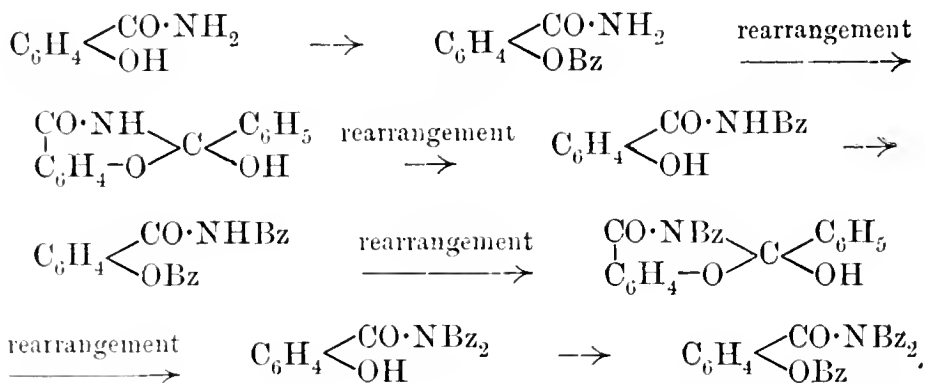
Tribenzoylsalicylamide, however, loses two benzoyl groups by this treatment, yielding Gerhardt's compound. There can be no doubt that the first action of the sulphuric acid is to eliminate the *O*-benzoyl group, and the abnormal separation of a second benzoyl group is in striking contrast to the complete stability of tribenzamide, dibenzamide, and acetylbenzamide towards concentrated sulphuric acid. The action is significant in pointing to a close relation which manifestly exists between the ortho-hydroxy- and *N*-benzoyl groups. The open chain compound $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CO} \cdot \text{NBz}_2 \\ \diagdown \text{OH} \end{array}$, formed as an intermediate product,

evidently at once closes to the isomeric ring, $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CO} \cdot \text{NBz} \\ \diagdown \text{O} \end{array} \text{C} \begin{array}{l} \diagup \text{C}_6\text{H}_5 \\ \diagdown \text{OH} \end{array}$, which in its turn opens and becomes *O,N*-dibenzoylsalicylamide, $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CO} \cdot \text{NHBz} \\ \diagdown \text{OBz} \end{array}$, the latter then undergoing normal hydrolysis. The

extremely easy conversion of tribenzoylsalicylamide into Gerhardt's compound in this manner is quite inexplicable on any other hypothesis (except, of course, that of free wandering of benzoyl groups) when it

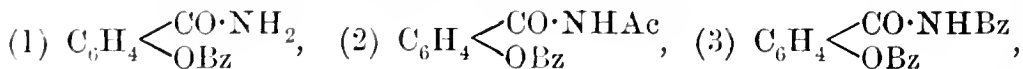
is remembered that this tribenzoyl derivative is quite stable towards alkali, and that tribenzamide resists even the action of boiling concentrated sulphuric acid.

Another striking feature which displays the close relation between the ortho-hydroxy- and *N*-acyl positions is the result of wet benzoylation of salicylamide, which successively gives (1) the monobenzoyl derivative, m. p. 144°; (2) Gerhardt's compound (by isomerisation); (3) the dibenzoyl derivative, m. p. 128°, and finally, as Einhorn (*loc. cit.*) has shown, (4) the tribenzoyl derivative, m. p. 188°. That is, all three available hydrogen atoms of salicylamide can be substituted by benzoyl on wet benzoylation. With benzamide, on the other hand, it is impossible to introduce even one benzoyl group in this way, and the quite unexpected result in the case of salicylamide can only be explained satisfactorily by assuming that owing to continual isomerisation there is always an OH group available which is benzoylated on the usual Schotten-Baumann lines, thus :



In respect to the unknown compound (b), $\begin{array}{c} \text{CO}\cdot\text{NBz} \\ | \\ \text{C}_6\text{H}_4\text{-O} \end{array} \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{OH} \end{array}$, attempts were made to obtain it by rearrangement, on heating, of *O*-*N*-dibenzoylsalicylamide, but, although evidence of some change was indicated by Titherley and Hicks, the authors have not been able definitely to isolate the ring isomeride.

Contrasting the rearrangement tendencies of the three substances :

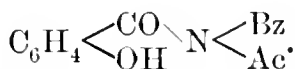
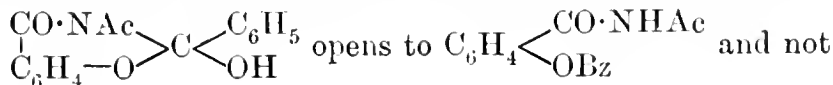


(1) rearranges to a very stable ring derivative (m. p. 208°), tautomeric with the open chain *N*-benzoyl derivative; (2) rearranges extremely easily to the ring isomeride (m. p. 106°), which, however, is unstable and readily reverts back to the original substance; whilst (3) on melting evidently rearranges to an equilibrium mixture of the original and ring isomeride, but the latter is apparently not capable of isolation owing to the extreme ease with which it reverts to the original com-

pound. From these observations it would appear that an acyl group attached to nitrogen renders the ring structure unstable. Moreover, when no acyl group is attached to nitrogen the ring has a tendency towards disruption, with formation of the *N*-acyl phenolic derivative, thus :



whilst when an acyl group is attached to nitrogen there is no tendency whatever to phenolic formation, as evidenced by the fact that



In general *N,N*-diacyl salicylamides appear to be too unstable to exist.

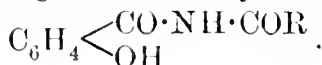
The compound $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO}\cdot\text{NHBz} \\ \text{OAc} \end{array}$ shows a less tendency to rearrange than does the isomeride $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO}\cdot\text{NHAc} \\ \text{OBz} \end{array}$, and the ring isomeride corresponding to the former, $\begin{array}{c} \text{CO}\cdot\text{NBz} \\ | \\ \text{C}_6\text{H}_4\text{--O} \end{array} \text{C} \begin{array}{c} \text{CH}_3 \\ \text{OH} \end{array}$, has not been isolated.

Apparently such methyl hydroxymetoxazone derivatives are less stable than the corresponding phenyl compounds, and this is emphasised in the contrast between the properties of the rearrangement products (m. p. 147° and 208° respectively) of *O*-acetyl- and *O*-benzoylsalicylamide. Evidence has been adduced to show that whilst the product melting at 147° is a true phenol, that melting at 208° is not, and it is manifest that the intermediate ring form, $\begin{array}{c} \text{CO}\cdot\text{NH} \\ | \\ \text{C}_6\text{H}_4\text{--O} \end{array} \text{C} \begin{array}{c} \text{CH}_3 \\ \text{OH} \end{array}$, derived from *O*-acetylsalicylamide, is very unstable and at once rearranges to *N*-acetylsalicylamide.

Similarly, the compound $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO}\cdot\text{NHBz} \\ \text{OAc} \end{array}$, on rearrangement with pyridine, owing to the instability of the intermediate methyl hydroxymetoxazone, gives the mixture of isomerides melting at 96° and 106° according to the mechanism given on p. 1326, a transformation which virtually amounts to a complete exchange of acyl groups.

Summary of Conclusions.

(1) *O*-Acyl salicylamides, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH}_2 \\ \text{O} \cdot \text{COR} \end{smallmatrix}$, are unstable and show a tendency to rearrange, giving a cyclic derivative, $\begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{C}_6\text{H}_4 - \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{R} \\ \text{OH} \end{smallmatrix}$, which may further rearrange to the *N*-acyl salicylamides,



(2) *N*-Acyl salicylamides, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{COR} \\ \text{OH} \end{smallmatrix}$, are also more or less unstable and show a tendency to rearrange forming the same ring derivative, $\begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{C}_6\text{H}_4 - \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{R} \\ \text{OH} \end{smallmatrix}$, which in its turn may open out giving the *O*-acyl salicylamides.

The stability of the intermediate ring form is less when R = methyl than when R = phenyl, and is less when the residual hydrogen of the nitrogen atom is replaced by an acyl group.

(3) Owing to the reversibility of these isomeric changes, acyl salicylamides in general are more or less labile substances and may undergo change on heating or dissolving in ionising solvents and sometimes even in non-ionising solvents like benzene and light petroleum. Among benzoyl derivatives, heating with glacial acetic acid favours the open chain formula with the benzoyl group attached to oxygen. Alkaline media also favour the open chain formula, but with the benzoyl group attached to nitrogen (and if a second acyl group is present it is eliminated). The phenomena are grouped under the title "metoxazone tautomerism."

(5) The possibility of individual existence of an *N*-acyl salicylamide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{R} \\ \text{OH} \end{smallmatrix}$, appears to depend on the nature of the acyl group. Thus, whilst *N*-acetylsalicylamide is stable, *N*-benzoylsalicylamide apparently exists only in the form of salts and derivatives, the free substance being tautomeric and behaving substantially as the cyclic derivative, $\begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{C}_6\text{H}_4 - \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \text{OH} \end{smallmatrix}$.

(6) *N*-*N*-Diacyl salicylamides, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CO} \cdot \text{R})_2 \\ \text{OH} \end{smallmatrix}$, are apparently too unstable to exist, the tendency to rearrange being so great as to lead to the isomeric derivative, $\begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CO} \cdot \text{R}) \\ \text{C}_6\text{H}_4 - \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{R} \\ \text{OH} \end{smallmatrix}$, which in its turn may rearrange to the open chain $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{R} \\ \text{O} \cdot \text{CO} \cdot \text{R} \end{smallmatrix}$.

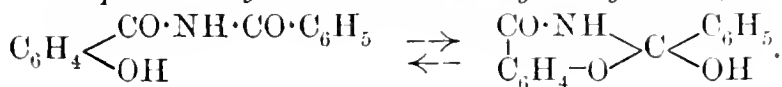
EXPERIMENTAL.

Preparation of O-Benzoylsalicylamide.

In addition to the method described by Titherley and Hicks (*loc. cit.*), this compound may be prepared (a) by low temperature pyridine-benzoylation of salicylamide, (b) by rearrangement of Gerhardt's benzoylsalicylamide by boiling with acetic acid.

(a) Salicylamide (139 grams) was dissolved in pyridine (280 grams) and cooled to -15° , and benzoyl chloride (140 grams) was added drop by drop with constant stirring; the addition of the benzoyl chloride occupied about three hours, and the mixture was then left for an hour at -15° . Dry ether (about 500 c.c.) was added and the whole agitated, by which means excess of pyridine was removed, leaving a semi-oily deposit of pyridine hydrochloride and *o*-benzoylsalicylamide. The ethereal solution was decanted and the residue treated with dilute sulphuric acid at 0° . The mass, which became granular, was stirred for five minutes, filtered, washed with water, and pressed. The product was nearly pure, and was recrystallised from toluene. A further quantity was recovered from the ethereal pyridine extract by shaking with dilute sulphuric acid. The yield was 89 per cent. of the calculated amount as compared with Titherley and Hicks' 40 per cent. by the wet method.

(b) One gram of Gerhardt's benzoylsalicylamide was boiled for four hours with 10 grams of glacial acetic acid; 0.3 gram unchanged substance separated on cooling and was filtered off. The filtrate, on diluting with water, yielded 0.5 gram of nearly pure *O*-benzoylsalicylamide melting at 141° ; after recrystallising from benzene it melted at 143° and solidified in the tube in the course of about thirty seconds.

Preparation of Gerhardt's Benzoylsalicylamide,

The authors have found that the best method of preparing this compound consists in boiling finely-powdered *O*-benzoylsalicylamide with fifty times its weight of water for fifteen minutes (compare Titherley and Hicks, *loc. cit.*). The product is nearly pure, and, without recrystallising, melts at 201° . The original method of Gerhardt and Chiozza gives only a 60 per cent. yield of an impure product difficult to recrystallise (compare Einhorn and Schupp, *loc. cit.*), whilst the other methods were found less convenient.

Decomposition with Ammonia.—One gram of Gerhardt's compound was heated with 20 c.c. of dilute ammonia in a sealed tube at 120° for an

hour; the yellow colour had then disappeared. The solution was concentrated to about half its bulk, filtered from a small quantity of salicylamide, which separated, and the filtrate was acidified; needles separated which melted, after recrystallising from water, at 108°. The product thus obtained was found to be a double compound of benzoic acid and salicylamide, and the same substance can be easily prepared by dissolving equimolecular proportions of its constituents in a large quantity of hot water. On cooling, it crystallises in long needles melting at 108—109°. It dissolves easily in dilute caustic soda; salicylamide is precipitated from the solution by saturating with carbon dioxide, whilst the filtrate yields benzoic acid on acidifying with dilute hydrochloric acid. Similar double compounds of benzamide with organic acids have been described by one of the authors (Titherley, *loc. cit.*, and *Trans.*, 1904, 85, 1673).

O-Methyl-*N*-benzoylsalicylamide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{O} \cdot \text{CH}_3 \end{smallmatrix}$, was obtained (*a*) by treating the silver salt of Gerhardt's benzoylsalicylamide with methyl iodide, (*b*) by benzoylation of *O*-methylsalicylamide.

(*a*) 10.5 grams of the silver salt (Limpricht, *Annalen*, 1856, 99, 249) were treated with 4.5 grams of methyl iodide in dry benzene solution and left for two days. The yellow silver salt disappeared and a mixture of silver iodide and *O*-methyl-*N*-benzoylsalicylamide separated. The solid was separated and washed with benzene; a small quantity of *O*-methyl-*N*-benzoylsalicylamide was precipitated from the benzene filtrate by adding light petroleum; the remainder was extracted from the silver iodide by hot alcohol, from which it crystallised on cooling.

0.2668 gave 13.6 c.c. nitrogen at 18° and 756 mm. $\text{N} = 5.85$.

$\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}$ requires $\text{N} = 5.49$ per cent.

(*b*) *O*-Methylsalicylamide, required for this synthesis, was described by Grimaux (*Bull. Soc. chim.*, 1895, 13, 26) and by Pinnow (*Ber.*, 1895, 28, 158). It is best obtained by an application of the potassium alkyl sulphate method (compare Titherley, *Trans.*, 1901, 79, 399) as follows: 13.7 grams of salicylamide and 15 grams of potassium methyl sulphate were added to a solution of 2.3 grams of sodium in the necessary amount of methyl alcohol. The methyl alcohol was evaporated and the residue was heated at 170° for fifteen minutes. When cold the solid mass was powdered and extracted with cold water. The insoluble solid was nearly pure *O*-methylsalicylamide; it was extracted with cold dilute caustic soda to remove salicylamide and subsequently recrystallised from water; the yield was 75 per cent. of the calculated.

Pyridine-benzoylation is not easily applicable to *O*-methylsalicylamide; the benzoyl derivative was prepared by the ester-sodiumacyl-

amide method (Titherley, Trans., 1904, 85, 1674). A mixture of 15 grams of *O*-methylsalicylamide and 0.4 gram of finely-powdered sodamide, moistened with benzene, was heated at 120–130° for two hours. The resulting sodium derivative was then moistened with pyridine and a saturated pyridine solution of 2 grams of phenol benzoate was added gradually, the mixture being frequently stirred and then left for twelve hours. The resulting mass was treated with dilute sulphuric acid, when an oily product separated, and this solidified on removing traces of benzene by a current of air. The solid, consisting of unchanged material and the benzoyl derivative, was digested with cold dilute caustic soda (in which the latter only is soluble) and quickly filtered into dilute hydrochloric acid. *O*-Methyl-*N*-benzoylsalicylamide separated and was recrystallised from alcohol, from which it was obtained in white, glistening needles.

Prepared by either of the above methods *O*-methyl-*N*-benzoylsalicylamide melts at 144–145°; it is sparingly soluble in ether, moderately so in cold alcohol or benzene, and readily soluble in chloroform, hot alcohol, or benzene. Although dissolving unchanged in cold dilute caustic soda, it is slowly hydrolysed on standing and the alkaline solution deposits benzamide, whilst *O*-methylsalicylic acid (m. p. 98°) may be precipitated from the filtrate by cold dilute hydrochloric acid.

O-Acetylsalicylamide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH}_2 \\ \diagdown \\ \text{O} \cdot \text{CO} \cdot \text{CH}_3 \end{smallmatrix}$, was obtained (a) by the action of ammonia gas on *O*-acetylsalicyl chloride, (b) by low temperature pyridine-acetylation of salicylamide.

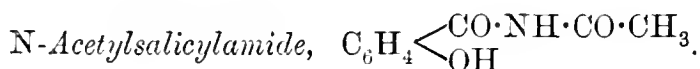
(a) The *O*-acetylsalicylchloride required was prepared by warming *O*-acetylsalicylic acid with thionyl chloride; on removing excess of the latter in a vacuum, the chloride remained as an oil. A solution of 9.5 grams of the chloride in absolute ether was saturated with dry ammonia gas. The precipitate, consisting of ammonium chloride and *O*-acetylsalicylamide, was separated, the ammonium chloride was removed by washing with water, and the acetylsalicylamide, after pressing on a porous plate, was recrystallised from ethyl acetate. Seventy per cent. of the theoretical yield was obtained.

(b) A solution of 13.7 grams of salicylamide in 27 grams of pyridine, kept at –15°, was treated with 7.9 grams of acetyl chloride, added drop by drop and with constant stirring; the mixture was left for thirty minutes at –15° and then stirred with 100 c.c. of ether. The ethereal solution was decanted, the semi-solid residue (which contains nearly all the acetylsalicylamide) stirred with dilute sulphuric acid at 0°, and the resulting granular mass was filtered, washed with water, and pressed on a porous plate. The product was almost pure and amounted to 81 per cent. of the calculated yield.

0.1449 gave 10.1 c.c. nitrogen at 22° and 756 mm. $N = 7.85$.

$C_9H_9O_3N$ requires $N = 7.83$ per cent.

O-Acetylsalicylamide, obtained by either of the above methods, melts at 138° and gives no ferric chloride reaction. It is sparingly soluble in ether, cold alcohol, or benzene, and easily so in hot alcohol with partial decomposition. It may be recrystallised from benzene or ethyl acetate and separates from the latter as transparent, prismatic crystals. It dissolves slowly in dilute ammonia, rapidly in dilute caustic soda, in each case with development of a slight yellow colour; on acidifying the ammoniacal solution, *N*-acetylsalicylamide (m. p. 148°) is precipitated; the caustic soda solution, however, rapidly loses its yellow colour, the acetylsalicylamide being almost immediately hydrolysed, giving salicylamide and acetic acid. *O*-Acetylsalicylamide is also rearranged to *N*-acetylsalicylamide on melting or by allowing it to stand in pyridine solution for a few hours. Cold concentrated sulphuric acid decomposes it immediately into acetic acid and salicylamide.



In addition to its formation from *O*-acetylsalicylamide under the conditions given above, *N*-acetylsalicylamide was obtained by direct action of acetyl chloride on salicylamide. 13.7 grams of salicylamide were heated in a reflux apparatus with 23.5 grams of acetyl chloride in a bath at 60° until the evolution of hydrogen chloride ceased. In this process, a chloro-derivative of acetylsalicylamide is formed (see below), and this is deposited as a white solid in the flask. The excess of acetyl chloride was drained off at the pump, the solid washed with light petroleum and dried in a vacuum. The chloro-derivative was converted into *N*-acetylsalicylamide by simple decomposition with cold water, and after thorough washing it was dried and recrystallised from benzene. The yield was 85 per cent. of the calculated.

0.1044 gave 7.2 c.c. nitrogen at 20° and 751 mm. $N = 7.80$.

$C_9H_9O_3N$ requires $N = 7.83$ per cent.

The cryoscopic determination of the molecular weight of *N*-acetylsalicylamide in both ethylene dibromide and glacial acetic acid gave results which varied both with concentration and the solvent. The extreme values obtained were M.W. = 133 and 204; $C_9H_9O_3N$ requires M.W. = 179. These abnormal results are consistent with the observations of Auwers and others on compounds containing a phenolic hydroxyl.

N-Acetylsalicylamide melts at 148°. It is sparingly soluble in ether

or cold benzene, moderately so in cold alcohol, and dissolves easily in hot alcohol, benzene, or chloroform; it is best recrystallised from benzene. With ethereal or alcoholic ferric chloride its solutions give an intense reddish-violet coloration. It dissolves in dilute aqueous ammonia with a pale yellow colour and is reprecipitated unchanged on acidifying; if left for twelve hours in ammoniacal solution, it is decomposed into salicylamide and acetamide. With dilute caustic soda, a sparingly soluble, pale yellow sodium salt first separates, but rapidly dissolves and undergoes hydrolytic decomposition. *N*-Acetylsalicylamide is not affected by cold strong sulphuric acid.

On treatment with hydrogen chloride, *N*-acetylsalicylamide forms a *chloro*-derivative, $C_9H_8O_2NCl$, the constitution of which has not yet been established. This compound is identical with that obtained directly by the action of acetyl chloride on salicylamide (see above), and was prepared as follows: 2 grams of *N*-acetylsalicylamide, dissolved and suspended in about 30 c.c. of chemically pure acetone, were treated with dry hydrogen chloride. The mixture became warm and clear, and then deposited the chloro-derivative as a white, crystalline powder, which was separated, washed thoroughly with absolute ether, and dried in a vacuum. It softens and decomposes at about 170° .

0.1263 gave 0.0911 AgCl. $Cl = 17.84$.

0.1896 „ 0.1354 AgCl. $Cl = 17.66$.

$C_9H_8O_2NCl$ requires $Cl = 17.72$ per cent.

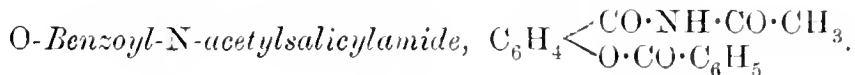
When aqueous silver nitrate is added to an ammoniacal solution of *N*-acetylsalicylamide, a very pale yellow *silver* salt is precipitated, which contains 1 atom of silver to 2 molecules of acetylsalicylamide.

0.2574 gave 0.0596 Ag. $Ag = 23.16$.

0.1997 „ 0.0465 Ag. $Ag = 23.22$.

$C_{18}H_{17}O_6N_2Ag$ requires $Ag = 23.28$ per cent.

The silver salt decomposes at 140° ; it is sparingly soluble in cold water or alcohol, but dissolves easily on heating.



This compound was prepared and described by Titherley and Hicks (*loc. cit.*), who obtained it by boiling *O*-benzoylsalicylamide with acetic anhydride. The authors have found that it can be obtained in an exactly similar manner by boiling Gerhardt's benzoylsalicylamide with acetic anhydride. It has also been obtained by the following methods:

(a) Pyridine-benzoylation of *N*-acetylsalicylamide at -15° : the most convenient method of preparation.

(b) Pyridine-benzoylation of *O*-acetylsalicylamide at -15° ; this process, depending on the slow rearrangement of the latter, gives only a small yield.

(c) Pyridine-acetylation of Gerhardt's benzoylsalicylamide at 0° by means of acetyl chloride.

(d) Rearrangement of its isomeride, m. p. 124° (*O*-acetyl-*N*-benzoylsalicylamide), by standing for twelve hours in pyridine solution.

(e) Rearrangement of its isomeride, m. p. 106° (*N*-acetyl-2:2-phenylhydroxybenzometoxazone), either by evaporating with acetic anhydride and crystallising from benzene and light petroleum, or by nucleating a dilute supersaturated light petroleum solution of the isomeride with a few needles of *O*-benzoyl-*N*-acetylsalicylamide.

Details only need be given of the preparation by one of these methods, namely (a): A solution of 17.9 grams of *N*-acetylsalicylamide in 35 grams of pyridine, kept at -15° , was treated gradually with 14 grams of benzoyl chloride with constant stirring; after standing thirty minutes at -15° , the pyridine mixture was agitated with about 100 c.c. of benzene. The benzene solution, containing pyridine hydrochloride in suspension, was shaken with dilute hydrochloric acid, washed with water, and dried with calcium chloride; on mixing with an equal volume of light petroleum, *O*-benzoyl-*N*-acetylsalicylamide slowly separated in large, transparent, prismatic crystals. These were filtered and washed with light petroleum. They weighed 28 grams, but contained 1 molecule of benzene of crystallisation to 2 molecules of the salicylamide derivative. These crystals, which melt at 94° , slowly lose benzene on standing at the ordinary temperature (rapidly at 80°), but at the same time they become opaque and are converted into the isomeric *N*-acetyl-2:2-phenylhydroxybenzometoxazone (m. p. 106°).

0.3500 lost 0.0429 at 80° . $C_6H_6 = 12.26$.

$(C_{16}H_{13}O_4N_2)_2, C_6H_6$ requires $C_6H_6 = 12.11$ per cent.

To obtain *O*-benzoyl-*N*-acetylsalicylamide free from benzene, the crystals were dissolved in boiling light petroleum, in which they are only sparingly soluble; 2 grams of the crystals required 1 litre of light petroleum (b. p. $70-120^{\circ}$), and the solution on cooling deposited *O*-benzoyl-*N*-acetylsalicylamide as a mass of transparent, silky, brittle needles, about 2 inches long, melting at 96.5° .

0.1879 gave 8.7 c.c. nitrogen at 23° and 766 mm. $N = 5.26$.

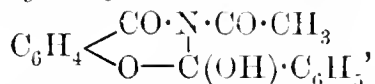
0.2194 in 57.63 ethylene dibromide gave $\Delta t = -0.16^{\circ}$. M.W. = 281.

$C_{16}H_{13}O_4N$ requires $N = 4.94$ per cent. and M.W. = 283.

A solubility determination gave the following: one litre solution in light petroleum, b. p. 43—50°, saturated at 25°, contained 0.450 grams.

The following may be added to the description of *O*-benzoyl-*N*-acetylsalicylamide given by Titherley and Hicks. On melting, it changes partially into the isomeric *N*-acetyl-2:2-phenylhydroxybenzometoxazone (m. p. 106°), and the change is practically complete if the liquid be kept at about 90° for a few minutes. The product slowly solidifies, and now melts at 104—105°. The long needles melting at 96.5° dissolve readily in benzene, and the saturated solution on standing a few minutes deposits the benzene-containing prismatic crystals. *O* Benzoyl-*N*-acetylsalicylamide dissolves in strong sulphuric acid with rapid hydrolysis, yielding benzoic acid and *N*-acetylsalicylamide. It is also rapidly hydrolysed by aqueous sodium or ammonium hydroxide, yielding acetic acid and Gerhardt's benzoylsalicylamide.

N-Acetyl-2:2-phenylhydroxybenzometoxazone,



was obtained from *O*-benzoyl-*N*-acetylsalicylamide (*a*) by heating it, or the crystalline form containing benzene, at 80° for several hours, (*b*) by dissolving it in boiling light petroleum and nucleating the solution with a trace of the metoxazone derivative. It is best prepared by the former method, the second method frequently giving rise to mixtures of the isomerides owing to incomplete rearrangement.

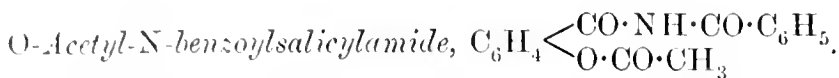
0.2353 gave 10.2 c.c. nitrogen at 21° and 761 mm. $\text{N} = 4.94$.

0.1991 in 57.89 ethylene dibromide gave $\Delta t = 0.145^\circ$. M.W. = 280.

$\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$ requires $\text{N} = 4.94$ per cent. and M.W. = 283.

A solubility determination gave the following: one litre solution in light petroleum, b. p. 40—50°, saturated at 25°, contained 0.432 grams (compare solubility of its isomeride).

The substance melts at 106°. It is moderately soluble in cold alcohol, benzene, or ether; it is easily soluble in hot alcohol or benzene and very readily so in chloroform. It crystallises from light petroleum in characteristic opaque, voluminous tufts. When a hot benzene solution of the metoxazone is allowed to cool, *O*-benzoyl-*N*-acetylsalicylamide crystallises in transparent, prismatic crystals containing benzene of crystallisation (see above). The metoxazone derivative gives no ferric chloride reaction, and all the chemical properties which have been examined are identical with those of *O*-benzoyl-*N*-acetylsalicylamide, and it is clear that it undergoes rearrangement to this compound with extreme ease.



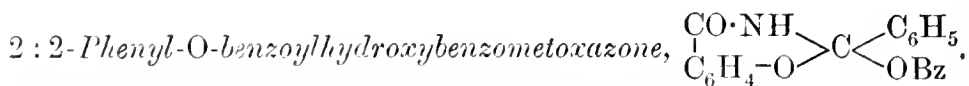
1.2 grams of Gerhardt's benzoylsalicylamide suspended and dissolved in 3 grams of pyridine was treated gradually with acetic anhydride at 0° until the solution was nearly clear. Ether was added, the resulting solution was filtered, and then extracted with dilute sulphuric acid to remove pyridine; during this operation, the acetyl derivative crystallised from the ethereal solution. It was filtered, and a further quantity was obtained by adding light petroleum to the ethereal filtrate. The product was purified by dissolving in acetone and precipitating with light petroleum; it melted at 124° and the yield was 85 per cent. of the theoretical.

0.1862 gave 8.3 c.c. nitrogen at 18° and 750 mm. $N = 5.09$.

$C_{16}H_{13}O_4N$ requires $N = 4.94$ per cent.

O-Acetyl-*N*-benzoylsalicylamide (m. p. 124°) is very sparingly soluble in ether or light petroleum, easily so in alcohol, acetone, chloroform, or hot benzene; from a mixture of acetone and light petroleum it crystallises in transparent, prismatic needles. It dissolves rapidly, with decomposition in aqueous ammonia or sodium hydrate, yielding a yellow solution from which Gerhardt's benzoylsalicylamide is precipitated on acidifying. It is soluble in cold strong sulphuric acid, with hydrolysis, yielding Gerhardt's compound and acetic acid.

When left for twelve hours in pyridine solution, this substance is completely converted into *O*-benzoyl-*N*-acetylsalicylamide, which was precipitated by adding excess of dilute sulphuric acid to the pyridine solution; the solid after being washed was recrystallised from light petroleum, when it melted at 96.5° .



Titherley and Hicks have shown (*loc. cit.*) that pyridine-benzoylation of Gerhardt's benzoylsalicylamide yields dibenzoylsalicylamide, $BzO \cdot C_6H_4 \cdot CO \cdot NH \cdot Bz$ (m. p. 128°); Einhorn and Schupp (*loc. cit.*) prepared the same compound by pyridine-benzoylation of salicylamide, using excess of benzoyl chloride.

When Gerhardt's benzoylsalicylamide is treated with benzoyl chloride in pyridine solution at -15° , two isomeric compounds result: (1) dibenzoylsalicylamide, m. p. 128° ; (2) the above compound, m. p. 160° .

Twelve grams of Gerhardt's benzoylsalicylamide, suspended and dissolved in 30 grams of pyridine, were treated gradually with 7 grams

of benzoyl chloride at -15° . The mass was left for two hours at -15° and then stirred with absolute ether. The ethereal solution was decanted and extracted with dilute sulphuric acid, when a solid (A) separated, which was filtered and dried; the semi-oily mass remaining in the flask was stirred with dilute sulphuric acid; it solidified, and the granular solid (B) was filtered and dried. A and B together weighed 18.5 grams; they were united and dissolved in boiling alcohol; on allowing to cool, needles separated, weighing 3.2 grams and melting at $140-150^{\circ}$, whilst dibenzoylsalicylamide, m. p. 128° , separated from the mother liquor on standing. The product, melting at $140-150^{\circ}$, on recrystallising from alcohol melted sharply at 160° .

0.2054 gave 7.8 c.c. nitrogen at 23° and 766 mm. $N = 4.31$.

$C_{21}H_{15}O_4N$ requires $N = 4.06$ per cent.

2:2-Phenyl-*O*-benzoylhydroxybenzometoxazone is sparingly soluble in alcohol, ether, or benzene, and moderately so in chloroform. It is very slowly decomposed by aqueous ammonia, yielding a yellow solution; it dissolves slowly in cold dilute sodium hydrate, rapidly on warming, giving benzoic acid and Gerhardt's benzoylsalicylamide. Cold strong sulphuric acid hydrolyses it to benzoic acid and Gerhardt's compound.

When subjected to pyridine-benzoylation, this compound was either recovered unchanged or decomposed, giving red resinous matter, according to the conditions of the experiment, and a benzoyl derivative has not yet been isolated.

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CXXXIII.—*Some New Derivatives of Dicyclopentadiene.*

By ALEXANDER RULE, M.Sc., Ph.D.

IN discussing the constitution of dicyclopentadiene, Kraemer and Spilker (*Ber.*, 1896, **29**, 552) described the nitrosochloride and the nitroso-compound. Several new derivatives of this hydrocarbon have recently been obtained by Wieland (*Ber.*, 1906, **39**, 1492), and it is therefore necessary to publish an account of some work done in the same field of research.

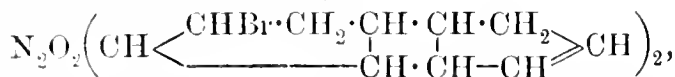
The compounds which are described in this paper were obtained during the years 1903–1904 in the laboratory of Prof. Knorr, at Jena,

and the work was carried out in conjunction with Prof. P. Duden. The author proposes to publish in a later paper an account of the action of nitrous gases on dicyclopentadiene, but by arrangement with Dr. Wieland, who is now engaged in research in the same direction, the publication is, for the present, postponed.

Nitroso-halogen Derivatives of Mono- and Di-cyclopentadiene.

The preparation of the nitrosochloride has already been described by Kraemer and Spilker (*Ber.*, 1896, 29, 552).

Dicyclopentadienenitrosobromide,



is obtained by treating a well-cooled, equimolecular mixture of dicyclopentadiene and amyl nitrite in acetic acid solution with a 50 per cent. solution of hydrogen bromide. The solution becomes intensely green, and after standing a short time a mass of crystals separates out. The substance is fairly soluble in hot benzene or chloroform, but sparingly so in other solvents. It can be recrystallised from chloroform, and when heated decomposes at 157°.

0.2203 gave 10.4 c.c. moist nitrogen at 14.5° and 752 mm. $\text{N} = 5.48$.

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Br}_2$ requires $\text{N} = 5.78$ per cent.

Dibromide of Dicyclopentadiene Nitrosobromide.—The nitrosobromide still contains an active double bond, as shown by its behaviour towards bromine. If a chloroform solution of the nitrosobromide is treated with excess of bromine and allowed to stand, or warmed on the water-bath, a crystalline bromo-addition product separates which is sparingly soluble in most organic solvents.

When recrystallised from amyl alcohol it is obtained in small plates melting at 211°.

0.1184 gave 0.1648 AgBr. $\text{Br} = 59.22$.

0.1909 „ 5.6 c.c. moist nitrogen at 14° and 736 mm. $\text{N} = 3.34$.

$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Br}_6$ requires $\text{Br} = 59.70$; $\text{N} = 3.48$ per cent.

For the sake of comparison with the nitrosohalogen derivatives of dicyclopentadiene, the corresponding compounds of monocyclopentadiene were also prepared.

Monocyclopentadiene Nitrosochloride, $\text{N}_2\text{O}_2\left(\text{CH}\left\langle\begin{array}{c} \text{CHCl}\cdot\text{CH} \\ \text{CH}_2--\text{CH} \end{array}\right\rangle\right)_2$ —

Monocyclopentadiene (5 grams) was mixed with amyl nitrite (8.8 grams) and well cooled in a freezing mixture. On adding the calculated quantity of alcoholic hydrochloric acid and shaking, the solution became bright green, and after a short time a mass of colourless crystals

separated, the colour of the solution at the same time changing to yellow.

The product must be filtered immediately and well washed with ether, as otherwise it becomes brown. The yield was 25—35 per cent. of the theoretical. The best results are obtained when not more than 5 grains of the hydrocarbon are worked up at one time. The nitrosochloride is easily soluble in chloroform and crystallises from alcohol or acetic acid in fine needles which, when heated, begin to darken at about 100° and decompose with slight explosion at 144°.

Prolonged heating of solutions of the substance results in the decomposition of a considerable portion. The raw product is very unstable, the presence of impurities causing it to darken in colour after standing for a short time.

0.2011 gave 0.3386 CO₂ and 0.0937 H₂O. C = 45.92 ; H = 5.17.

0.1501 gave 14.1 c.c. moist nitrogen at 19° and 747 mm. N = 10.61.

0.1180 „ 0.1293 AgCl. Cl = 27.10.

C₁₀H₁₂O₂N₂Cl₂ requires C = 45.62 ; H = 4.56 ; N = 10.64 ; Cl = 26.99 per cent.

Monocyclopentadiene nitrosobromide is quite similar to the nitrosochloride, but less difficult to obtain in the pure state.

0.1809 gave 11.9 c.c. moist nitrogen at 15° and 761 mm. N = 7.71.

C₁₀H₁₂O₂N₂Br₂ requires N = 7.95 per cent.

Both substances give Liebermann's reaction, but, unlike the corresponding derivatives of *dicyclopentadiene*, they are unstable and very readily decomposed on warming with alkalis.

They give resinous products with bases such as ammonia, aniline, pyridine, and piperidine, and show a very slight tendency to unite with bromine or react with halogen acids.

Dicyclopentadiene nitrosochloride and nitrosobromide behave in general like the terpene nitrosochlorides described by Wallach and others. They are, however, only very slowly attacked by alcoholic potash and sodium ethylate, much resin being formed at the same time.

When heated with aniline, oximes are not formed as in the case of the terpene nitrosochlorides, but resinous products and amidoazobenzene result.

Conversion of Nitroso-halogen Compounds into Oxime Derivatives.

Ethoryisonitrosodicyclopentadiene, $C_5H_6 \begin{matrix} \text{CH} & \text{---} & \text{CH}_2 \\ | & & | \\ \text{CH} & \cdot & \text{CH(OEt)} \end{matrix} > C:NOH.$

—One molecule of the nitrosobromide is heated with excess of an

alcoholic solution of sodium ethylate until all the solid has disappeared. The alcohol is removed from the alkaline solution by distillation and dilute sulphuric acid added, when an oil mixed with resinous matter is precipitated. The product is purified by extracting with ether and then with light petroleum, in which most of the resin is insoluble. After standing for some time over sulphuric acid, the oxime solidifies to a crystalline mass which melts at a low temperature, and can be recrystallised from light petroleum.

0.1916 gave 11.3 c.c. moist nitrogen at 18° and 745 mm. $N = 6.65$.

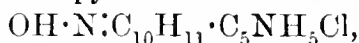
$C_{12}H_{17}O_2N$ requires $N = 6.76$ per cent.

The compound is precipitated from its alkaline solution by carbon dioxide as an oil, which slowly solidifies. The alkaline solution strongly reduces Fehling's solution.

The yield of pure product was very small, and a further investigation of its reactions, especially the isolation of the ketone, was not attempted.

A second method for obtaining oxime derivatives was afforded by the action of pyridine on the nitroso-halogens.

Nitrosodi *cyclopentadiene* pyridinium chloride,



was prepared by Wieland. The author obtained it by carefully heating 10 grams of nitrosochloride with 45—50 c.c. of pyridine in a flask fitted with a reflux condenser. When the boiling point of the pyridine is reached, a violent reaction takes place, the solution becomes brown, and the nitrosochloride is momentarily dissolved; the pyridinium salt then begins to crystallise out, and the whole mass solidifies to a firm cake. Yield, about 80 per cent. of the theoretical. For analysis, the product was extracted several times with chloroform to remove traces of pyridine hydrochloride.

0.2006 gave 17.9 c.c. moist nitrogen at 19.5° and 749 mm. $N = 10.08$.

$C_{15}H_{17}ON_2Cl$ requires $N = 10.12$ per cent.

The salt is somewhat hygroscopic; on heating it darkens at 180° and melts at 211° (Wieland gives 218°).

Nitrosodicyclopentadiene pyridinium bromide is prepared in an analogous way from the nitrosobromide. It can be recrystallised from water, forming small cubes which darken at 200°.

0.1657 gave 0.0958 AgBr. $Br = 24.60$.

$C_{15}H_{17}ON_2Br$ requires $Br = 24.92$ per cent.

Both pyridinium salts darken in colour when warmed with potassium carbonate, baryta, or caustic soda solution; a resin separates, and an odour of pyridine is apparent. The preparation of the oxime was

therefore carried out as follows: the aqueous solution of the pyridine salt is freed from halogen by treatment with the calculated quantity of moist silver oxide. The solution becomes strongly alkaline, and a small quantity of silver oxide is dissolved; since the latter is reduced on warming the solution and causes the formation of resin, it is necessary to remove the silver by passing hydrogen sulphide through the solution. After filtering off the silver sulphide, a clear, yellow solution is obtained, which, on warming on the water-bath, becomes cloudy, and a yellow, amorphous product separates. It is advisable to discontinue the warming as soon as the product coagulates.

The liquid is extracted with ether, the yellow residue from the ethereal solution dissolved in a little caustic soda, and the alkaline solution filtered from resin and precipitated by carbon dioxide. The amorphous product can be further purified by dissolving it in benzene and reprecipitating with light petroleum. A white, amorphous product is obtained, which is easily soluble in most organic solvents and melts at 110° .

0.1837 gave 0.4530 CO_2 and 0.1181 H_2O . $\text{C} = 67.25$; $\text{H} = 7.14$.

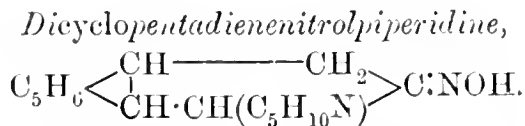
0.2141 „ 14.3 c.c. moist nitrogen at 18° and 754 mm. $\text{N} = 7.65$.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 67.06$; $\text{H} = 7.26$; $\text{N} = 7.82$ per cent.

According to the above figures the substance is the *oxime* of dicyclopentenolone (oxynitrosodicyclopentadiene), the ethyl ester of which has already been described above.

The oxime gives an oily sodium salt on treatment with concentrated caustic soda; it is only slowly attacked on boiling with dilute acids, resin being formed at the same time, so that the isolation of the ketone was not possible. Other attempts to convert the oxime into crystalline derivatives were unsuccessful.

This method for the preparation of oxime derivatives is also unsatisfactory on account of the poor yield.



Kraemer and Spilker (*loc. cit.*) have already shown that piperidine reacts vigorously with dicyclopentadiene nitrosochloride. The reaction is less violent if carried out in toluene solution, using 2 molecules of piperidine for each molecule of nitrosochloride. The solution is raised to the boiling point, when the reaction takes place, then allowed to cool, and the piperidine hydrochloride which separates out is filtered. On concentrating the toluene solution and cooling, an almost theoretical yield of the piperidine derivative is obtained. Lustrous plates separate

which melt at 157° (Kraemer and Spilker give 160°) and decompose on being heated to a higher temperature.

0.1768 gave 0.4717 CO_2 and 0.1416 H_2O . $\text{C} = 72.76$; $\text{H} = 8.89$.

0.1020 " 9.9 c.c. moist nitrogen at 13.5° and 743 mm. $\text{N} = 11.18$.

$\text{C}_{15}\text{H}_{22}\text{ON}_2$ requires $\text{C} = 73.01$; $\text{H} = 8.94$; $\text{N} = 11.38$ per cent.

The base is easily soluble in most organic solvents, but sparingly so in water. It is not volatile in steam. As a nitrolamine it is at the same time a weak acid, and when precipitated in an oily condition from acid solutions by an alkali, it is soluble in excess of the reagent, but in the crystalline form is much less soluble.

The *hydrochloride* of the piperidine base is sparingly soluble in water, and separates in white crystals. It is nearly insoluble in concentrated hydrochloric acid, and this property can be made use of in identifying the base.

0.1562 gave 0.0802 AgCl . $\text{Cl} = 12.70$.

$\text{C}_{15}\text{H}_{23}\text{ON}_2\text{Cl}$ requires $\text{Cl} = 12.56$ per cent.

The *picrate* of the base separates on treating an alcoholic solution of the base with the calculated amount of picric acid. When recrystallised from hot water it is obtained in short, yellow needles which melt without decomposition at 147° .

0.1319 gave 16.35 c.c. moist nitrogen at 13° and 753 mm. $\text{N} = 14.51$.

$\text{C}_{21}\text{H}_{25}\text{O}_8\text{N}_5$ requires $\text{N} = 14.73$ per cent.

The piperidine derivative is very stable towards dilute acids; no change takes place on heating for a short time with concentrated hydrochloric or sulphuric acid, but prolonged heating causes the formation of resin. In the circumstances, the elimination of hydroxylamine or the conversion of the oxime into an unsaturated nitrile could not be induced.

Reducing agents act only with difficulty on the piperidine base. Five grams of the base were dissolved in absolute alcohol and treated with a large excess of sodium, but the greater part remained unchanged, and could be easily recognised by the formation of the sparingly soluble hydrochloride. At the same time, however, a *diamine* base was formed as a thick oil crystallising with difficulty. It was separated by dissolving the mixture of bases in a little concentrated hydrochloric acid. On cooling the solution with ice, the hydrochloride of the piperidine base separated almost completely. From the filtrate the diamine base was precipitated by alkali, dissolved in ether, and converted into the hydrochloride.

The *hydrochloride* of the diamine base is a white, crystalline substance, very soluble in water and concentrated hydrochloric acid.

0.1372 gave 10.45 c.c. moist nitrogen at 11.5° and 748 mm. $N = 8.90$.

$C_{15}H_{26}N_2Cl_2$ requires $N = 9.18$ per cent.

The *platinichloride* of the diamine base is obtained when an aqueous solution of the hydrochloride is treated with platinic chloride, and separates in round, crystalline aggregates which melt at 249° with decomposition.

0.2009 gave 0.0605 Pt. $Pt = 30.11$.

0.2047 „ 8.3 c.c. moist nitrogen at 13.75° and 745 mm. $N = 4.69$.

$C_{15}H_{26}N_2Cl_6Pt$ requires $Pt = 30.29$; $N = 4.36$ per cent.

THE ORGANIC LABORATORIES,
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CXXXIV.—*Thiocarbamide as a Solvent for Gold.*

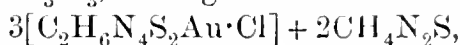
By JAMES MOIR, M.A., D.Sc.

It has been recently shown (Proc., 1906, 22, 105) that gold slowly dissolves in acid solutions of thiocarbamide, and that solution takes place with remarkable rapidity in the presence of suitable oxidising agents.

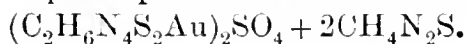
Since then, two new complex gold salts have been isolated from these solutions, and an attempt has been made to ascertain their constitution.

The new sulphate and chloride were obtained by dissolving precipitated gold in solutions of thiocarbamide acidified with sulphuric or hydrochloric acid respectively, the action being accelerated by the addition of hydrogen peroxide. They have approximately the composition of addition-compounds of thiocarbamide with aurous salts, namely, $Au_2SO_4 + 6CH_4N_2S$ and $AuCl + 2\frac{2}{3}CH_4N_2S$; in this respect they are analogous to the series of double-salts of the heavy metals, such as $CuCl + 3CH_4N_2S$, described by Emerson Reynolds and others.

The author considers, however, that the chloride has in reality the formula $C_8H_{26}N_{16}S_8Au_3Cl_3$, having some such constitution as

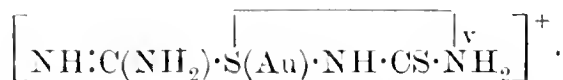


and infers that the sulphate possesses a similar formula, namely,

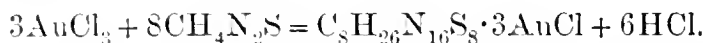


In the latter case, however, the analytical evidence is incomplete, owing to the difficulty of preparing the substance, and the formula must be taken as only tentative. In the case of the chloride, on the

other hand, the evidence is clear that there is a smaller proportion of hydrogen in the compound than is required by the supposition that it is merely an addition-compound of AuCl and $\text{CH}_4\text{N}_2\text{S}$. It is probable that the cation $\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{Au}$ has the constitution



The complex chloride can also be obtained from the product of the reaction between potassium aurichloride and thiocarbamide, a fact which supports the formula which is proposed for it, as the following equation shows:



It is converted, by boiling with strong hydrochloric acid, into the compound $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, first described by Emerson Reynolds (*Annalen*, 1869, 150, 255).

These three complex gold salts behave so differently from ordinary aurous compounds that one is compelled to assume the existence in them of a complex cation such as $\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{Au}$, an assumption supported by analogy, since the properties of such salts as cuprous thiocarbamide carbonate and sulphate (*Ber.*, 1884, 17, 300, for example, $\text{Cu}_2\text{SO}_4 + 5\text{CH}_4\text{N}_2\text{S} + 2\text{H}_2\text{O}$ *) show that copper, at least, does not react in the usual way when combined with thiocarbamide. The author is inclined to suspect that most of these so-called addition-compounds of thiocarbamide and salts of the heavy metals are constituted similarly to his new gold compound, and thus contain less hydrogen than is indicated by the accepted formulæ.

The action of *s*-diphenyl- and diacetyl-thiocarbamide on gold was tried, but the results were negative. Hence it is probable that the activity of thiocarbamide itself depends on its isomerisation to



the hydrogen of the -SH group being replaceable by gold, just as in the recently-discovered gold mercaptides (*Ber.*, 1905, 38, 2813).

EXPERIMENTAL.

(a) *Preparation of Gold-thiocarbamide Sulphate.*

Finely-divided gold, prepared from auric chloride and ferrous sulphate, was added to a strong solution of thiocarbamide acidified with sulphuric acid. The action was accelerated by occasional addition of hydrogen peroxide and warming to 50° . The filtered solution was allowed to evaporate spontaneously, when opaque, white rosettes of the complex sulphate crystallised. These were recrystallised for

* Beilstein (1, 1317) formulates this substance incorrectly as $\text{Cu}_2(\text{SO}_4)_2$, &c.

analysis, and dried for several hours at the temperature of boiling water (94.5°), thereby losing water of crystallisation, which was not determined. The substance then melted without decomposition at 161° .

On careful ignition, 0.1327 gave 0.0550 Au. Au = 41.45.

$\text{Au}_2\text{SO}_4 + 6\text{CH}_4\text{N}_2\text{S}$ requires Au = 41.64.

$(\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{Au})_2\text{SO}_4 + 2\text{CH}_4\text{N}_2\text{S}$ requires Au = 41.82 per cent.

(b) *Preparation of Gold-thiocarbamide Chloride.*

(1) *From Gold.*—Exactly the same method as the above was employed, using hydrochloric instead of sulphuric acid. The product formed large, colourless, six-sided plates or lozenges possessing a waxy lustre and striated parallel to the longer diagonal, which is also the direction of extinction of polarised light.

It melts at 190° without decomposition, which, however, begins at about 210° (see p. 1349). It is alkaline to litmus, as is Reynolds' compound, $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, and contains chlorine, but no cyanogen or sulphocyanogen.

After drying in the steam-bath :

0.14775 gave 0.0671 Au. Au = 45.42 per cent.

(2) *From Gold Chloride.*—To a strong solution of thiocarbamide at 50° , a solution of gold potassium chloride was added until the red precipitate ceased to redissolve. The resulting pale yellow solution was warmed for an hour, when it became nearly colourless; a little sulphur was deposited and was separated. On standing overnight, a good yield of the hexahedral compound was obtained, identical with that prepared by the former method. As this method is simple, it was possible to prepare a fair quantity of the substance for exhaustive analysis. It should be noted, however, that it is essential to use gold potassium chloride and not chloroauric acid, since the latter gives Reynolds' compound, $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, instead of the hexahedral compound.

0.1322 gave 0.0600 Au. Au = 45.39.

0.0474 „ 0.0216 Au. Au = 45.50.

0.3370 „ 0.1532 Au. Au = 45.46.

Average, allowing for difference of quantity used, Au = 45.44 per cent.

0.2125 gave 0.0690 AgCl. Cl = 8.03.

0.2125 „ 0.2178 BaSO_4 . Soluble S = 14.08.

0.2135 „ 0.3106 BaSO_4 . Total S = 19.97 per cent.

Total sulphur was determined by digesting with aqua regia and precipitating as BaSO_4 .

From these figures, the atomic ratio $\text{Au} : \text{Cl} = 1 : 0.983$, that is, 1 : 1. The ratio $\text{Au} : \text{total S} = 1 : 2.703$, which is most probably 3 : 8.

The simplest formula for this substance would be $3\text{AuCl} + 8\text{CH}_4\text{N}_2\text{S}$, which requires $\text{Au} = 45.26$ per cent., but an error of even so little as 0.2 per cent. in excess is nearly impossible in the mean of four estimations of gold by ignition.

The formula which I propose for the compound, namely,

$$3(\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{AuCl}) + 2\text{CH}_4\text{N}_2\text{S},$$
 requires $\text{Au} = 45.47$; $\text{Cl} = 8.17$; $\text{S} = 19.72$ per cent.

It is just possible, however, that the discrepancy is due to an error in the accepted atomic weight of gold, and that the substance really possesses the formula $3\text{AuCl} + 8\text{CH}_4\text{N}_2\text{S}$.

(c) *Conversion of the Hexahedral Chloride into Reynolds' Compound.*

On boiling the hexahedral compound for a minute with strong hydrochloric acid and separating from a little sulphur, lustrous, opaque, white needles, agreeing exactly with Reynolds' compound, were obtained on cooling. After being recrystallised and dried in the steam oven, 0.0534 gave 0.0273 Au. $\text{Au} = 51.2$; $\text{C}_2\text{H}_8\text{N}_4\text{ClS}_2\text{Au}$ requires $\text{Au} = 51.24$ per cent.

(d) *Action of Caustic Alkali on the Hexahedral Chloride.*

On adding sodium hydroxide to the aqueous solution of the compound, an orange, gelatinous precipitate is obtained, which on warming becomes denser and dark olive-green. This product is identical with that obtained by Rathke (*Ber.*, 1884, 17, 307) by the action of ammonia on Reynolds' compound, $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, and amounted to 114 per cent. of the gold obtained by ignition (whereas Rathke's specimen amounted to 116 per cent.).* I find, with Rathke, that it seems to contain carbon and nitrogen as well as sulphur. The most probable constitution is $\text{Au}_2\text{S} + \text{CH}_3\text{N}_2\text{SAu}$, the theoretical amount of which is 118 per cent. of the contained gold.

The colourless filtrate contained the whole of the chlorine and the rest of the sulphur; the chlorine was estimated by precipitating with silver nitrate, extracting the precipitate with ammonia, and reprecipitating with nitric acid. This procedure was necessitated by the

* Another specimen, made by the use of ammonia instead of sodium hydroxide, was analysed:

0.0611 gave 0.0521 Au. $\text{Au} = 85.27$.

$\text{CH}_3\text{N}_2\text{S}_2\text{Au}_3$ requires $\text{Au} = 84.67$ per cent.

fact that the original substance gives a complex precipitate with silver nitrate (see below). The residual silver sulphide was converted into barium sulphate, whereby the "soluble sulphur" of the analyses was determined. From the difference between "total" and "soluble" sulphur, the sulphur contained in the olive-green gold precipitate is calculated as 5.89 per cent. of the original, which is a little too high for that required by the formula suggested for the olive compound, but the determination of soluble sulphur by this circuitous process is probably inaccurate.

(e) *Effect of Heat on the Chloride.*

On heating in the air-bath at 210° to constant weight, the product was uniform and dark brown, and amounted to 148.6 per cent. of the gold obtained by ignition. It appears to be a single substance, and the only probable formula is $\text{Au}_3\text{S}_2 \cdot 3\text{CH}_3\text{N}_2\text{S}$, which corresponds to 148.7 per cent. of the contained gold.

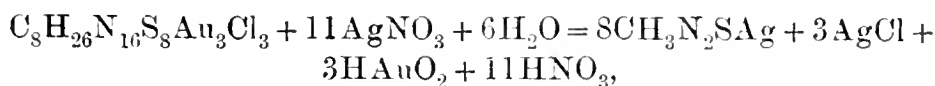
(f) *Action of Silver Nitrate.*

On adding silver nitrate in excess to a solution of the substance, an immediate brown precipitate of auric hydrate mixed with silver chloride is obtained, followed after a few seconds by a bulky mass of felted white needles of silver-thiocarbamide, whereby the whole is made to gelatinise. This operation was carried out quantitatively and the results agree with the complicated formula which I put forward for the gold thiocarbamide chloride.

The whole was diluted with very weak nitric acid, the precipitate filtered and dried at 60° for an hour, and finally left for a week over sulphuric acid in a vacuum. The filtrate contained a little dissolved silver thiocarbamide, the amount of which was determined by conversion into silver sulphide and this was added to the main quantity.

0.4280 gave 0.7543 mixed product and 0.0885 Ag_2S ($= 0.0653$ gram $\text{CH}_3\text{N}_2\text{SAg}$, or 1.08 mols.). Total $\text{Au} + \text{AgCl} + \text{CH}_3\text{N}_2\text{SAg} = 0.8196$ gram, or 191.5 per cent. of the original.

The theoretical equation is :



whence 1301 grams should yield 8 mols. of silver thiocarbamide, 3 mols. of silver chloride, and 3 atoms of gold (on drying); total 191.2 per cent. of the original substance taken. This agreement between theory and experiment was confirmed by the subsequent

treatment of the precipitate, which was first ignited, then fully chlorinated and re-ignited, and finally reduced to gold-silver alloy.

Ignition: Theory for $3\text{Au} + 3\text{AgCl} + 6\cdot92$, $\text{Ag} = 0\cdot5811$ gram.
 Found $0\cdot5856$ gram.

Chlorination: Theory for $3\text{Au} + 9\cdot92$, $\text{AgCl} = 0\cdot6584$ gram. Found $0\cdot6410$ gram.

Alloy: Theory for 3Au + 9·92, Ag = 0·5466 gram. Found 0·5450 gram.

I desire to thank Mr. H. Harding, B.Sc., for his kindness in supplying me with the necessary extracts from chemical literature inaccessible in this country.

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MINES DEPARTMENT,
TRANSVAAL.

CXXXV.—*The Vapour Pressures of Binary Mixtures.*
Part 1. The Possible Types of Vapour Pressure
Curves.

By ARTHUR MARSHALL.

THE relationship between the vapour pressures of the components of a mixture of two liquids is given by the simple expression :

[illegible]

in which p_1, p_2 are the partial pressures exerted by the two substances 1 and 2, and x is the molecular proportion of the substance 1 present in the liquid mixture, that is, the number of gram-molecules of the substance 1 divided by that of 1 and 2 together; $(1 - x)$ is consequently the molecular proportion of the substance 2. This equation, which refers to changes taking place at constant temperature, has been worked out independently by Duhem (*Ann. de l'École Normale sup.*, 1887, (iii), 4, 9; *Traité élém. de Mécanique chimique*, 1889, 4, chap. 7), Leffeldt (*Phil. Mag.*, 1895, 40, 397), Margules (*Sitzungsber. K. Akad. Wien.*, 1895, 104, 1243), and Ostwald. A very simple and convincing proof has been published by Luther (see Ostwald, *Allg. Chemie*, 1902, 2, ii, 639), and the experimental investigations of Zawidski have fully confirmed its accuracy (*Zeit. physikal. Chem.*, 1900, 35, 129).

The vapour pressures of binary mixtures have been discussed in

some detail in the text-books of Ostwald (*loc. cit.*, pp. 611—666, 687—699), Duhem (*Méchan. chimique*, 4, 194—221), and Roozeboom (*Heterogenen Gleichgewichte*, 1904, 2, 8—57), consequently in this communication attention will be confined mostly to points in which the treatment of the subject, as presented in the works cited, requires amplification or correction. Mention of most of the original papers on the subject will be found in the communication of Zawidski (*loc. cit.*) and in Young's work on Fractional Distillation (London, 1903).

Before proceeding to discuss the question of the different types of curves it is necessary to define some of the terms used.

In all curves the pressures are supposed to be plotted as normals against the values of x , which is equal to $N_1/N_1 + N_2$, where N_1 , N_2 are the number of gram-molecules of each of the two substances present in the liquid mixture.

A *point of inflection* is a point where a pressure curve changes its direction of curvature, that is, where the second differential of the pressure with regard to x is equal to zero.

A *type* of curve is distinguished by the number of points of inflection and of maxima and minima (points where $dP/dx = 0$) it possesses and by the order in which they occur.

Possible Types of Partial Pressure Curves.

Equation (i) may for convenience be written in the form

$$\frac{dp_1}{dx} \frac{x}{p} = - \frac{dp_2}{dx} \frac{1-x}{p_2} \quad \dots \quad (ii),$$

and from this conclusions may at once be drawn as to the shapes of the partial pressure curves. When one substance is present in large excess, the partial pressures p_1 of the other substance generally follow Henry's law approximately if not accurately. That is,

$$\frac{dp_1}{dx} = C = \frac{p_1}{x} \quad \text{and} \quad \frac{dp_1}{dx} \frac{x}{p_1} = 1,$$

and graphically the partial pressures are represented by a straight line through the zero point. From equation (ii) it is evident that in this case the vapour pressures of the substance present in excess obey a similar law,

$$\frac{dp_2}{dx} \frac{p_2}{1-x} = -1 \quad \text{or} \quad \frac{dp_2}{dx} = - \frac{p_2}{1-x},$$

which is merely a mathematical expression of Raoult's law, and shows that the partial pressures of the second substance are represented graphically by a curve tangential to the diagonal π_1 I (Fig. 1).

When the two substances possess normal molecular weights in the liquid state, that is, when the molecular weights are the same as those in the gaseous state, the laws of Raoult and Henry hold with approximate accuracy over a considerable range. When, however, the molecules of either substance, or of both, associate, or when they tend to form complexes such as hydrates, the vapour pressures obey these laws through a smaller range only; nevertheless, the laws do, as a rule, hold good approximately for solutions in which one or other of the two substances greatly preponderates. The only exceptions which have hitherto been clearly recognised are aqueous solutions of electrolytes. But this exception is exactly what would be anticipated from the usually accepted theories of mass action and electrolytic dissociation (see Gahl, *Zeit. physikal. Chem.*, 1900, 33, 178).

As regards the course of the middle portion of the partial pressure curves, Ostwald has assumed that there is only one change of direction of curvature, and consequently only one point of inflection. The experimental data which have been accumulated since Ostwald's theory was published have fully justified his assumption, for in no case where the partial pressures have actually been measured with accuracy do they show more than one point of inflection. Theoretical considerations also would lead one to expect that there would not be more than one point of inflection in any ordinary case. For whatever action there may be between the various molecules in the liquid phase, one would anticipate that if the ratio p_1/x be greater than π_1 at any one point, at no other point will it be less than π_1 , and if at any one point it be less than π_1 , at no other point will it be greater. The value of p_1/x may therefore be expected to increase or decrease continuously until at the upper end of the curve it becomes equal to π_1 . But if such be the case, it is not possible to draw a partial pressure curve with more than one point of inflection. As already stated, no partial pressure curves which have hitherto been determined by direct experiment show more than one point of inflection, but in the case of dilute solutions of sulphur trioxide in water, although the necessary vapour pressure measurements are wanting, the freezing-point determinations made by Pickering (*Trans.*, 1890, 57, 331) indicate that there must be two points of inflection. This case is, however, extremely complex, for not only is the acid electrolytically dissociated, but it combines with the water in several different proportions, the water itself associates, and the sulphur trioxide dissociates in the gaseous state into sulphur dioxide and oxygen (see Gahl, *loc. cit.*). In other electrolytic solutions the phenomena are more simple, and this anomalous course of the vapour pressure curves apparently does not occur.

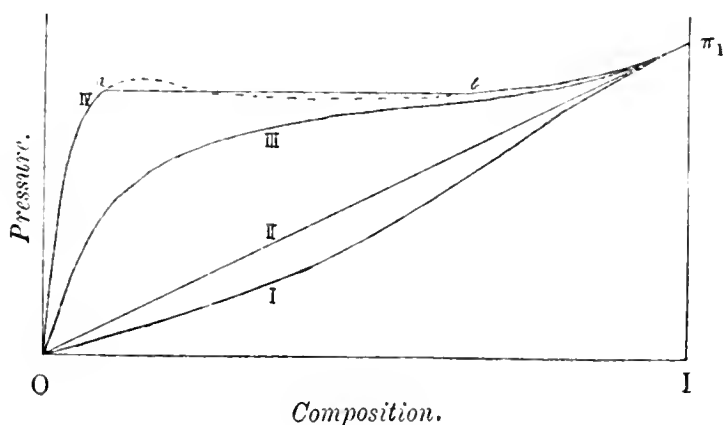
In their central proportions, the vapour pressure curves of electro-

lytic solutions probably do not differ materially in general form from those of non-electrolytes, but as experimental data are almost entirely lacking the present communication will be confined to the discussion of non-electrolytic mixtures.

The four possible types of partial pressure curves are shown in Fig. 1. The simplest type is the straight line, type II, which, however, appears only to occur when there is no contraction and no change of temperature on mixing the two substances.

When the two substances have a tendency to combine chemically, the partial pressure curves are usually of type I, but this type can also occur when there is no chemical combination. Amongst cases which have hitherto been investigated, type III is the most common, especially when the molecules of one or both substances associate in the liquid state. The existence of curves of this type does not, however, necessarily imply that association takes place, for mixtures

FIG. 1.



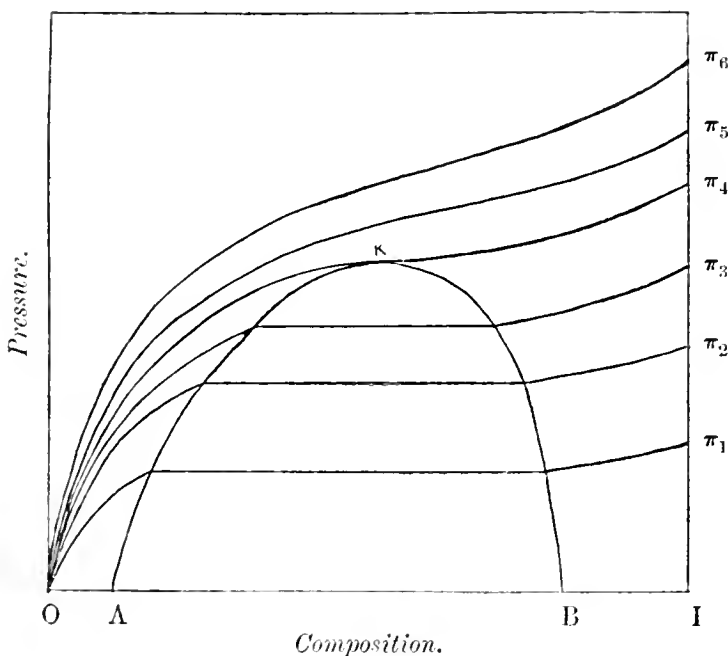
of benzene and hexane fall into this category ; nor does the existence of a curve of another type prove that association does not take place.

These three types are not sharply distinguished one from the other ; on the contrary, curves can show every degree of curvature from the one extreme, as represented by pyridine and acetic acid belonging to type I, through the straight line to the other extreme, as represented by such pairs of liquids as hexane and methyl alcohol belonging to type III, and beyond into the region of the curves belonging to type IV. The straight line is, in fact, only a special case intermediate between type I and type III, but its practical importance is so great that it was considered advisable to place it in a class by itself, for already many pairs of substances have been found to give curves which are straight lines within the limits of experimental error, and this not merely at one temperature, but probably throughout a considerable range.

When the two substances are not miscible in all proportions, the partial pressure curves assume the form IV of Fig. 1. As has been pointed out by Ostwald, a fall of partial pressure with an increase of concentration would involve a condition essentially unstable. A solution which showed such a phenomenon could not exist, but would at once decompose in two layers corresponding in composition and pressure with the points *a* and *b*. These two layers must have not only the same total pressure, but also the same partial pressures.

The gradual change of a partial pressure curve of type III with change of temperature into one of type IV is shown in Fig. 2, in which the curve *AKB* represents the partial pressures at the limits of solubility at various temperatures. The mixture has a solubility

FIG. 2.



critical point *K*, at which it is evident the partial pressure curve is horizontal. Below the critical point, each partial pressure curve has a maximum and minimum value of *x* for a certain pressure; above it the curves rise throughout.

The analogy between the curves of type IV and those given by the equation of state of van der Waals has already been commented on by Duhem, Margules, and others; the analogy, indeed, amounts almost to identity. In the case of the partial pressures of mixtures of methyl ethyl ketone and water investigated by myself (see experimental part), I endeavoured to fit to the experimental curves equations of the form:

$$(p_1 + ax^2)\left(\frac{1}{x} - b\right) = S,$$

where a , b , and S are constant. But although the general form of the curve is given by such an equation, it is not possible to represent the observations accurately throughout the whole course. In view of the fact that, even in the far less complex case of a simple substance, van der Waals' equation gives a qualitative rather than a quantitative picture of the behaviour, it was hardly to be expected that greater success would be achieved in this case, where there are two substances and three phases and complications arising from changes of density and surface tension.

Mutual Relationship of the Two Partial Pressure Curves.

In accordance with equation (i), the two partial pressure curves must always be of the same type. This fact has been pointed out by Ostwald, who has also remarked that if the vapour pressures exerted by the substances in the pure state be equal, the two curves will be equal in all respects (*Allg. Chem.*, 2, p. 641). If the pressures be different, he proceeds to say, "so ist die eine Kurve in solchem Sinne ein Spiegelabbild der anderen, dass zwar der senkrechte Massstab verschieden ist, die Zeichen des ersten und zweiten *Differentialquotienten* aber stets entgegengesetzt sind, auch beide daher *gleichzeitig durch Null gehen*. Es wiederhold sich mit anderen Worten der Gang der ersten Teilkurve bezüglich des Steigens oder Fallens, und *bezüglich der konvexen und der konkaven Krümmung, so wie des Wendepunktes* an der zweiten Teilkurve, nur in anderem Massstabe." Part of this statement is undoubtedly correct, but the portion which I have italicised will be shown to hold good only in a special case, namely, at the critical solution temperature.

If equation (ii) be differentiated with regard to x , it gives

$$\frac{d^2p_1}{dx^2} = -\frac{d^2p_2}{dx^2} \cdot \frac{1-x}{x} \cdot \frac{p_1}{p_2} - \frac{dp_1}{dx} \cdot \frac{1}{p_1(1-x)} \left\{ \frac{p_1}{x} - \frac{dp_1}{dx} \right\} \quad \text{. . . (iii),}$$

and when $\frac{d^2p_1}{dx^2} = 0$, we have

$$\begin{aligned} \frac{d^2p_2}{dx^2} &= -\frac{xp_2}{p_1^2(1-x)} \cdot \frac{dp_1}{dx} \left\{ \frac{p_1}{x} - \frac{dp_1}{dx} \right\} \\ &= \frac{1}{p_1(1-x)} \frac{dp_2}{dx} \left\{ \frac{p_1}{x} - \frac{dp_1}{dx} \right\} \quad \text{. (iv)} \end{aligned}$$

Of the factors on the left-hand side of equation (iv), $\frac{1}{p_1(1-x)}$ must always be a positive quantity; $\frac{dp_2}{dx}$ is always negative, except in a part of the unrealisable central portion of curves of type IV; $\left\{ \frac{p_1}{x} - \frac{dp_1}{dx} \right\}$ is always negative with a curve of type I, it is equal to 0

with a curve of type II, and it is positive with curves of types III and IV. It is evident, then, that at the point of inflection of the p_1 curve the second differential of the p_2 curve is positive in the case of type I, negative in the case of type III, and positive in the case of type IV. In the case of type II, there is no curvature and consequently no change of direction of curvature. It may be shown in the same way that $\frac{d^2p_2}{dx^2}$ alters its sign in a similar manner. Ostwald's statement that the points of inflection fall on the same normal is not true therefore; on the contrary, with curves of type I and III, the points of inflection are nearer to the upper parts of the curves, and with curves of type IV they are nearer to the points where the partial pressures are equal to 0.

At the critical solution point $\frac{dp_1}{dx} = 0$, consequently

$$\frac{d^2p_1}{dx^2} \cdot \frac{x}{p_1} + \frac{d^2p_2}{dx^2} \cdot \frac{1-x}{p_2} = 0.$$

Therefore, if the second differential of one curve disappear at this point, that of the other must do so too. Reference to Fig. 2 will show that both partial pressure curves must have points of inflection at the critical point. Ostwald's statement is therefore correct in this special case, and in this only.

From equation (ii), it is evident that with curves of type IV the maximum of the first curve occurs at the same composition as the minimum of the second, and the minimum of the first at the same composition as the maximum of the second.

Total Pressure Curves.

The possible forms of partial pressure curve have now been discussed, and it has been shown that they all belong to four types, which, however, are only special forms of a general type. The next stage is to ascertain what forms of total pressure curve can be obtained by combining two partial pressure curves of the same type. For this purpose, use can be made of the equations:

$$P = p_1 + p_2 \quad \dots \dots \dots \quad \text{(v)},$$

$$dP = dp_1 + dp_2 \quad \dots \dots \dots \quad \text{(vi)},$$

$$d^2P = d^2p_1 + d^2p_2 \quad \dots \dots \dots \quad \text{(vii)},$$

which are so obvious that no proof is required.

Combining (ii) and (v), we obtain

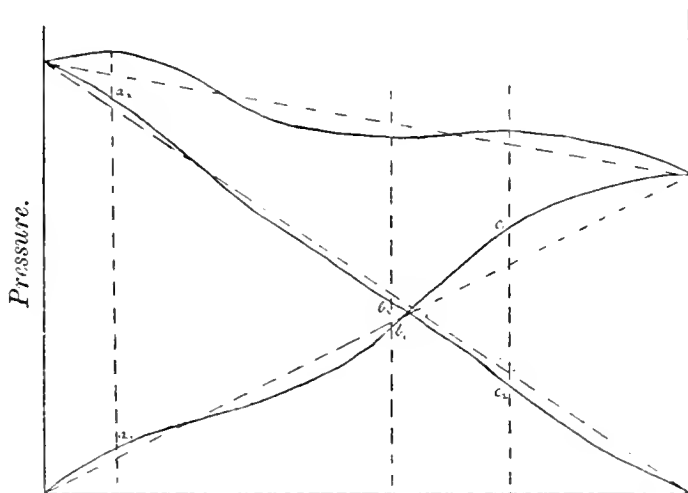
$$\frac{dP}{dx} = \frac{dp_2}{dx} \left(1 - \frac{p_1}{p_2} \cdot \frac{1-x}{x} \right) \quad \dots \dots \dots \quad \text{(viii)},$$

which shows that P is at a maximum or minimum when either $\frac{dp_2}{dx} = 0$ or $\frac{p_1}{p_2} = \frac{x}{1-x}$.

One or the other of these two conditions must be fulfilled whenever $\frac{dP}{dx} = 0$. The first of these conditions occurs only in the unrealisable portion of curves of type IV, the second is the condition of a mixture of constant boiling point (compare Margules, *loc. cit.*).

It has been suggested by Ostwald (*loc. cit.*, pp. 618, 642) that with pairs of liquids miscible in all proportions the total pressure curve may have two maxima and a minimum or two minima and a maximum. He has suggested that the former may occur when the vapour pressures of the two constituents are not very different and the temperature is not far removed from that of the critical point. Zawidski, on the

FIG. 3.



other hand, has suggested that the latter may occur when the two constituents associate and also combine chemically one with the other. It can, however, be demonstrated that only one maximum or minimum can occur in a total pressure curve when the two substances are miscible in all proportions.

For, if possible, let the total pressure curve have two maxima and a minimum as in Fig. 3. Then at each of the points where $\frac{dP}{dx} = 0$,

$\frac{p_1}{p_2} = \frac{x}{1-x}$. The partial pressure curves must therefore pass through the points a_1, b_1, c_1 and a_2, b_2, c_2 respectively. But this is inconsistent with the equation (ii) and with the law of Raoult and Henry.

Similarly, it may be shown that two minima and a maximum are equally impossible. One minimum or one maximum is therefore all

that is possible in total pressure curves of types I or III. With curves of type II no maximum or minimum can of course occur.

If equation (viii) be differentiated with regard to x , we obtain

$$\frac{d^2P}{dx^2} = \frac{d^2p_2}{dx^2} \left(1 - \frac{p_1}{p_2} \cdot \frac{1-x}{x}\right) + \frac{dp_2}{dx} \cdot \frac{1}{xp_2} \left(\frac{p_1}{x} - \frac{dp_1}{dx}\right) \quad \dots \quad (\text{ix}).$$

$$\text{Let } \frac{d^2p_2}{dx^2} \left(1 - \frac{p_1}{p_2} \cdot \frac{1-x}{x}\right) = \alpha \quad \dots \quad (\text{x}),$$

$$\text{and } \frac{dp_2}{dx} \cdot \frac{1}{xp_2} \left(\frac{p_1}{x} - \frac{dp_1}{dx}\right) = \beta \quad \dots \quad (\text{xi}),$$

$$\text{then } \frac{d^2P}{dx^2} = \alpha + \beta \quad \dots \quad (\text{xii}).$$

Of the factors that appear in equation (ix), x , $(1-x)$, p_1 , p_2 are all necessarily positive. The sign of $\frac{d^2p_2}{dx^2}$ has been discussed above; that of $\left(1 - \frac{p_1}{p_2} \cdot \frac{1-x}{x}\right)$ is shown by equation (viii) to be always negative when dP/dp_2 is negative, that is, when the slope of the total pressure curve is opposite to that of p_2 curve. It is positive when dP/dp_2 is positive, and is equal to 0 when a constant boiling mixture is formed. The first differential dp_2/dx is always negative except in a part of the unrealisable portion of the curve of type IV. The factor $\left(\frac{p_1}{x} - \frac{dp_1}{dx}\right)$ is always negative with a curve of type I, and always positive with those of types III and IV. The possible variations of all the factors in equation (ix) being known, the possible variations in the sign of the second differential d^2P/dx^2 can be summed up. The signs of all the variable factors are given in Table I. In all cases it is supposed that vapour pressure of the second substance in the pure state is higher than that of the first. In those instances where several signs are given, the curve is supposed to be divided into portions at the points of inflection or at a maximum or minimum. The brackets in the column referring to type IV are to mark off the unrealisable portions of the curves. The letter (a) means that no constant boiling mixture is formed, (b) indicates that a constant boiling mixture is formed.

TABLE I.

	Type I.	Type III.	Type IV.
$\alpha \left\{ \begin{array}{l} \frac{d^2 p_2}{dx^2} \dots\dots\dots \\ \left(1 - \frac{p_1}{p_2} \cdot \frac{1-x}{x} \right) \end{array} \right.$	- +	+ -	+(+ -) -
Sign the same as that of $\frac{dP}{dp_2}$ in realisable portion of all curves.			
$\beta \left\{ \begin{array}{l} \frac{dp_2}{dx} \dots\dots\dots \\ \left(\frac{p_1}{x} - \frac{dp_1}{dx} \right) \dots\dots \end{array} \right.$	-	-	-(- + -) -
$\alpha \left\{ \begin{array}{l} a \dots\dots\dots \\ b \dots\dots\dots \end{array} \right.$	+ - -	- + +	-(- +) +
$\beta \dots\dots\dots$	+	-	-(- + -) -
$\frac{d^2 P}{dx^2} \left\{ \begin{array}{l} a \dots\dots\dots \\ b \dots\dots\dots \end{array} \right.$	+ + \pm	- - \pm	-(- + \pm) \pm
$\frac{d^2 P}{dx^2} \left\{ \begin{array}{l} a \dots\dots\dots \\ b \dots\dots\dots \end{array} \right.$	\pm + \pm	- - \pm -	-(- + -) -

Consideration of the facts assembled in Table I shows that twelve possible types of total pressure may occur. The first and second differentials of these are given in Table II, and in Figs. 4 to 8 the shape of each is shown graphically.

TABLE II.

Type.	$\frac{dp_1}{dx}$	$\frac{d^2 p_1}{dx^2}$	$\frac{dP}{dx}$	$\frac{d^2 P}{dx^2}$	Points of inflection.	Max. ima.	Min. ima.
IA. } IB. } IC. } ID. }	+	+	$\left\{ \begin{array}{l} + \\ + \\ - + \\ - + \end{array} \right.$	$\left\{ \begin{array}{l} + + - \\ + + + \\ + + + \\ - + - \end{array} \right.$	1 0 0 2	0 0 0 0	0 0 1 1
II. }			+	0	0	0	0
IIIA. } IIIB. } IIIC. } IIID. }			$\left\{ \begin{array}{l} + \\ + \\ + - \\ + - \end{array} \right.$	$\left\{ \begin{array}{l} - - + \\ - - - \\ - - - \\ - - + - \end{array} \right.$	1 0 0 2	0 0 1 1	0 0 0 3
IVA. } IVB. } IVC. }			$\left\{ \begin{array}{l} +(+ - +) + \\ +(+ - +) + - \\ +(+ - + -) - \end{array} \right.$	$\left\{ \begin{array}{l} -(- +) + \\ -(- + -) - \\ -(- + -) - \end{array} \right.$	1 2 2	2 2 1	1 1 1

Type IA.—Curves of this type occur when the two substances have very different vapour pressures. Trinitroglycerol and acetone, the figures relating to which will be found in the experimental portion of this paper, form an example of it. Other instances are ammonia and water, glycerol and water, ether and aniline (Raoult, *Zeit. physikal. Chem.*, 1900, 36, 60).

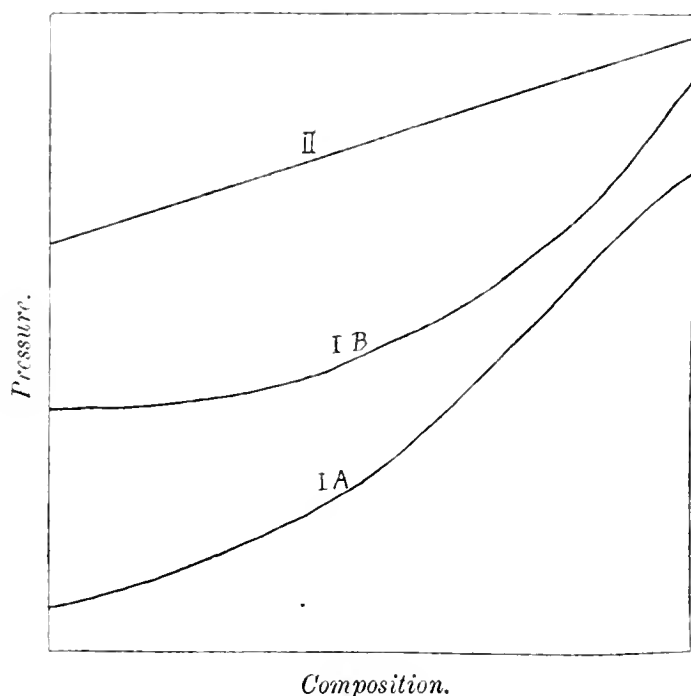
Type IB calls for no special comment. An example is presented by mixtures of carbon tetrachloride and toluene investigated by Lehfeldt (*Phil. Mag.*, 1898, v, 46, 42). Also chloroform and benzene, and carbon tetrachloride and ether investigated by Linebarger.

Type IC.—Mixtures of acetone and chloroform give a total pressure curve of this form (Zawidski, Linebarger, *J. Amer. Chem. Soc.*, 1895, 17, 615, 690).

Type ID.—For a well-established instance of this type we are again

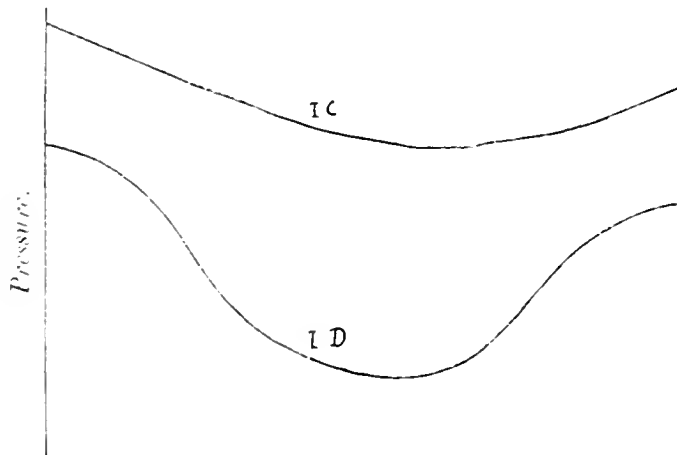
indebted to Zawidski, who found it to occur with mixtures of pyridine and acetic acid. Mixtures of water with the strong mineral acids also

FIG. 4.



appear to give curves of this type, but full experimental data are wanting. The double change of curvature combined with a minimum

FIG. 5.



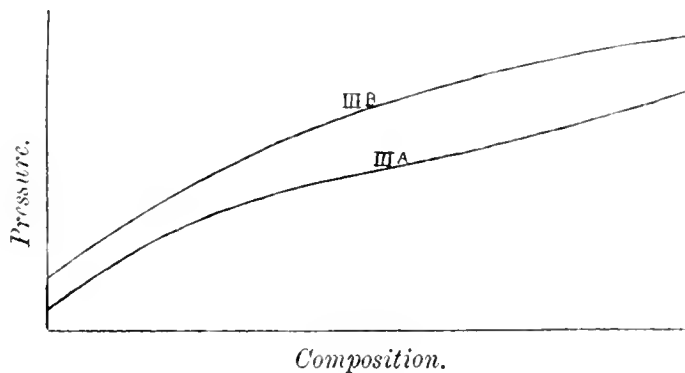
probably only occurs when the two substances have considerable tendency to combine with one another.

Type II has been well discussed by Young and others. It will suffice here to mention that Zawidski gives a list of seven binary

mixtures which have straight vapour pressure curves, and that Young has added two mixtures (chlorobenzene and bromobenzene, and methyl and ethyl alcohol) for which the pressure-composition line is quite straight, and four others (ethyl propionate and acetate, ethyl benzene and toluene, *n*-octane and *n*-hexane, and toluene and benzene) for which the curvature is exceedingly slight (Trans., 1902, 81, 768 ; 83, 45).

Type IIIA, like *IIA*, occurs when the vapour pressures of the pure substances are very different. Instances are acetone and water (Taylor, *J. Physical Chem.*, 1900, 4, 360 ; Schreinemakers, *Zeit. physikal. Chem.*, 1901, 39, 486) ; aniline and alcohol (Guthrie, *Phil. Mag.*, 1884, [v], 18, 511) ; ether with turpentine, nitrobenzene, aniline, methyl salicylate, and ethyl benzoate (Raoult, *Zeit. physikal. Chem.*, 1888, 2, 353 ; recalculated by Linebarger, *J. Amer. Chem. Soc.*,

FIG. 6.



1895, 17, 699) ; carbon tetrachloride and nitrobenzene (Linebarger, *loc. cit.*).

Type IIIB is common. The following may be mentioned as examples : acetic acid and benzene, carbon tetrachloride and benzene (Zawidski, *loc. cit.*).

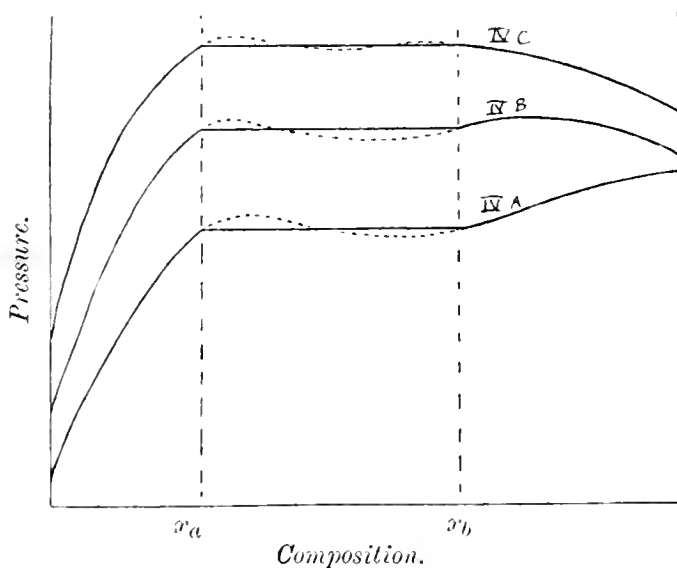
Type IIIC is also very common. Amongst the mixtures investigated by Zawidski, carbon tetrachloride and ethyl acetate, ethyl iodide and ethyl acetate, carbon disulphide and methylal, carbon disulphide and acetone may be mentioned as belonging to this class (see Fig. 8).

Type IIID probably only occurs with any given mixture within a limited range of temperature in the neighbourhood of the solution critical point. Mixtures of phenol and water give curves of this type at temperatures from the critical point, 68°, up to 90°, and probably somewhat beyond (see Schreinemakers, *Zeit. physikal. Chem.*, 1900, 35, 474). It may be regarded as a transition stage between types *IIIC* and *IVB*, and will be discussed later (see Fig. 8).

Type IVA occurs when the substances are not miscible in all pro-

portions, and the one is very volatile compared with the other. According to a statement of Baneroff's (*Phase Rule*, 1897, p. 101), solutions of sulphur in benzene and toluene give total vapour pressures of this type. Some rough qualitative experiments with sulphur dioxide in water appear to indicate that they fall within this category. As in all cases where the vapour pressure of one substance is small, the total pressure curve necessarily almost coincides with the partial pressure curve of the other constituent. All that has been said concerning the gradual change of a partial pressure curve of type III into one of type IV may be repeated with regard to the change of a total pressure curve of type IIIA into one of IVA, and the conversion may be illustrated by a diagram almost identical with Fig. 2. When a mixture of this type is submitted to fractional distillation, it will

FIG. 7.



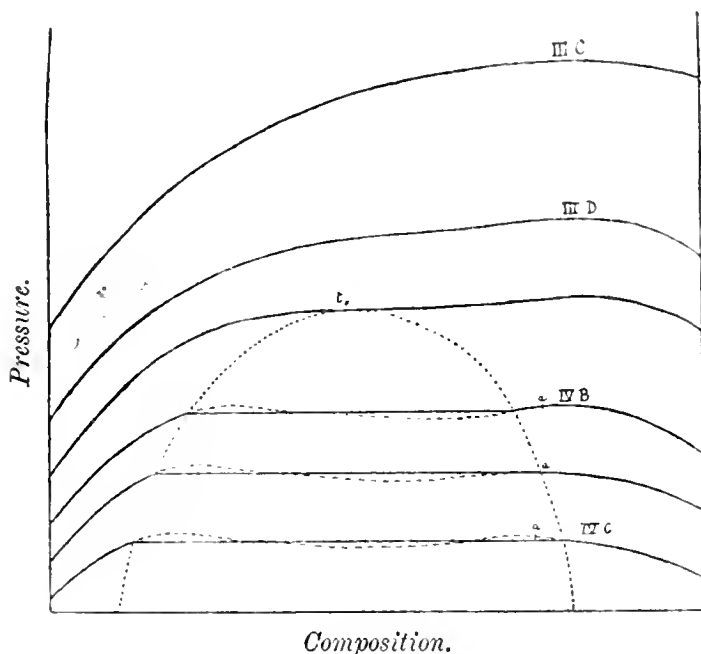
ultimately be resolved entirely into the two pure constituents, just as in a case where the total pressure curve rises throughout. At the two limiting compositions x_a , x_b , not only are the total pressures the same, but the partial pressures also, and consequently the composition of the vapour given off from a liquid of the composition x_a must lie between x_b and the point where $x=1$.

Type IV B.—Ostwald in his discussion of the vapour pressures of binary mixtures omitted to mention this type. Nevertheless, it appears to be a common one, for Schreinemakers has found that mixtures of phenol and water below the solution critical point give curves belonging to it, and three pairs of liquids examined by me do so also: these three pairs are methyl ethyl ketone and water, ethyl acetate and water, ether and water, experimental data of which are given later. The gradual change of a curve of type IV B into one of type IIID

and then IIIC is shown in Fig. 8. The second point of inflection may fall either within or without the unrealisable area.

Type IVC.—There are many pairs of liquids which give curves of this type, but the mixtures of water and aniline which were investigated by Schreinemakers (*loc. cit.*) form the only case for which vapour tension measurements extending over the whole range of compositions are available. A few determinations with mixtures of amyl alcohol and water have been made by myself and will be found in the experimental portion of this communication. For the gradual alteration of the total pressure curve with change of temperature up to the critical point, Ostwald gives a diagram which is reproduced in Fig. 9. There is, however, no proof that the critical point t_k is also the point of

FIG. 8.



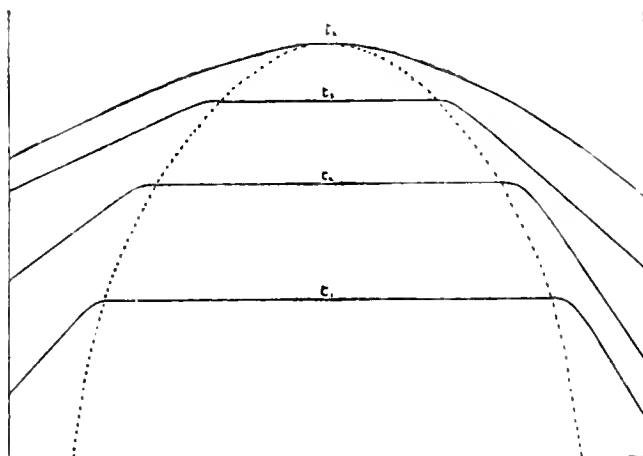
maximum vapour pressure, and it is more probable that, as the mutual solubility rises, the point where $\frac{p_1}{p_2} = \frac{x}{1-x}$ approaches nearer and nearer to the solubility curve, and eventually passes it, so that the curve becomes one of type IVB. The further metamorphoses of the curve are consequently those shown in Fig. 8.

Referring to the diagram (Fig. 9), Ostwald says (*loc. cit.*, p. 693): "Verfolgt man nun . . . die Kurven abwärts, indem man vom kritischen Punkte ausgeht, so wird man vermuten dürfen, dass die Stelle, der die Zusammensetzung des Dampfes entspricht, immer noch einen ausgezeichneten Punkt bezüglich der Teildruckkurven darstellt. Die horizontale Tangente des Maximalpunktes geht in die empirische Dampfdruckgerade des heterogenen Gebietes über, welche die theore-

tischen Einzeldruckkurven in drei Punkten schneidet. Zwei von diesen Punkten haben die phys-ische Bedeutung, dass sie die Zusammensetzung der beiden Flüssigkeiten angeben, bei welchen die Unstetigkeit der empirischen Kurve eintritt. Man darf daher vermuten, dass auch der dritte Durchschnittspunkt eine physische Bedeutung haben wird, und da bleibt nur die Zusammensetzung des Dampfes hierfür übrig."

Such a method of reasoning is evidently a dangerous one. There is no proof that the two partial pressure curves are intersected by the empirical straight lines at the same values of x , and when Fig. 8 is substituted for Fig. 9 the argument fails entirely. In endeavouring to ascertain the composition of the vapour given off by the heterogeneous mixture, there is no reason to use any other methods than would be employed with curves of other types. The composition of the vapour

FIG. 9.



must always lie somewhere between that of the maximum total pressure (where $\frac{p_1}{p_2} = \frac{x}{1-x}$), and that of the liquid phase nearer to the upper portion of the curve. The approximate positions of the points which represent the composition of the vapour phase are marked a in Fig. 8.

In Figs. 7 and 8, only critical solution points of maximum temperature have been represented. It has been shown by Rothmund (*Zeit. physikal. Chem.*, 1898, 26, 433) that in some cases the mutual solubility of two substances increases with falling temperature until finally they become entirely miscible. So far as I have been able to foresee, there would be no essential difference in the variations of the shape of the vapour pressure curves, whether the critical solution point be of minimum or maximum temperature.

The changes that curves of type IV undergo have been discussed in

some detail on account of their theoretical importance. Total pressure curves of other types also alter their shapes with variations of temperature, and probably any one type may under suitable conditions gradually change into any other. These possibilities will not, however, be considered in the present communication.

It is a fortunate circumstance that although the number of binary mixtures the vapour pressures of which have been thoroughly investigated is not large, nevertheless there is not one of the twelve types which has not a representative.

Regnault's Law.

Prof. Duhem, to whom we are indebted for the original discovery of the fundamental equation (i), has investigated many of the problems connected with the vapour pressure of binary mixtures (*Mécanique Chimique*, 1899, 4, 1—228). The greater part of Duhem's work does not, however, directly concern the subject of this communication. But on p. 204 he calls attention to some of the experiments which Regnault carried out with ether and water. The latter took a mixture of equal volume of these substances, which of course was in two layers, and determined the pressure of the saturated vapour given off by the mixture. He found that at each temperature this pressure was almost equal to that of the saturated vapour of anhydrous ether. The following table (III) gives the results.

TABLE III.

Temperature.	Vapour pressures		Difference.
	Of mixture.	Of pure ether.	
15·56°	362·95	361·4	+ 1·5
20·40	440·32	440·0	+ 0·3
24·21	510·08	510·0	+ 0·1
26·73	562·79	563·6	- 0·8
27·99	589·38	590·0	- 0·6
33·08	710·02	711·6	- 1·6

Duhem confidently predicted that amongst partially miscible liquids other cases of a similar nature would be discovered, and this has indeed been the case. Schreinemakers found that at a temperature of 56·3° solutions of phenol in water have the following vapour pressures :

TABLE IV.

Phenol.	Pressure.
0 per cent.	125 mm.
2·0 "	125 "
5·58 "	127 "
7·42 "	126·5 "
10·88 "	127 "
14·5 "	126 "
60·0 "	126 "

} Liquid separates
into two layers.

and my own experiments with mixtures of methyl acetate and water give somewhat similar results (see below).

Duhem, from the behaviour of mixtures of ether and water, deduced a rule which he calls Regnault's law, and enunciates as follows: "La Tension de la vapeur mixte émise par le mélange que forme le liquide 2, en se dissolvant dans le liquide 1, est sensiblement égale, à toute température, à la tension de vapeur saturée du liquide 1." Regnault's law is, however, only a rough approximation. Even with mixtures of ether and water the divergence from the "law" is considerable. This is shown not merely by the boiling point experiments which have been performed by Beckmann (*Zeit. physikal. Chem.*, 1891, 8, 134), Linebarger (*ibid.*, 1895, 17, 500), and myself (see below), but also by a very simple distillation experiment. It has been pointed out by Duhem that a mixture which obeys Regnault's law should give off vapour having the same composition as the liquid, and that when the liquid separates into two layers the vapour should have the same composition as the layer which is richer in the more volatile constituent. Water is distinctly more soluble in ether at its boiling point than at the ordinary temperature, as is shown by the fact that if a boiling saturated solution of water in ether be cooled it becomes decidedly cloudy. Consequently a heterogeneous mixture of ether and water should, according to the "law," yield, on distillation, a distillate which is cloudy at the ordinary temperature. Experiment shows that this is not so; on the contrary, a constant boiling mixture of water and ether is obtained which is perfectly clear at all ordinary temperatures.

Even in cases where the vapour pressure of the heterogeneous liquid is quite different from that of the more volatile constituents, there is, however, a tendency for the curve in the neighbourhood of solubility to approximate to a horizontal straight line. This fact is brought out by Schreinemaker's measurements of the vapour pressures of mixtures of aniline and water at 75°, which are given in Table V.

TABLE V.

Aniline.	Vapour pressure.
0 per cent.	289 mm.
1.38 "	297 "
2.88 "	300 "
3.46 "	301 "
3.49 "	301 "
4.18 "	301 "
4.6 "	302 "
4.7 "	302 "
4.85 "	302 "
{ 5.2 "	303 " }
{ 94.0 "	303 " }
	Liquid separates into two layers.

My own experiments with methyl ethyl ketone and water illustrate this tendency even more clearly. In Fig. 12, the boiling-point curve

ABC is not to be distinguished from a straight line between the compositions 95 per cent. and 85 per cent., but at $A'B'C'$, Fig. 13, the temperatures are plotted on a scale many times as large, and the true nature of the curves can be seen.

The reason why the total vapour pressure curve tends to approximate to a straight line in these cases is not difficult to see. The first differentials of the partial pressure curves are here small, for at a point not far distant within the unrealisable area they disappear; they are also of opposite sign. As dP/dx , the first differential of the total pressure curve, is equal to their algebraical sum, it also must be small. The second differential, d^2P/dx^2 , must be small too, because at about the same level of pressure there are two points of inflection where it disappears altogether. Hence, although the total pressure curve in this neighbourhood is never a horizontal straight line, it may at first sight appear to be one.

Methods of Determining Total Pressure Curves.

In considering the subject theoretically, the partial pressure curves were discussed first and then the total pressure curves. This was the most convenient arrangement, because the number of possible types of partial pressure curves is smaller, and the types of total pressure curves may be derived from them. When the course of a curve is to be ascertained, however, it is nearly always necessary to ascertain the total pressures first, and derive the partial pressures from them either experimentally or by mathematical analysis. It will be best, therefore, now to consider the methods of determining the total pressures, and then to discuss how the partial pressures may be derived from them.

In order to be able to plot vapour pressures against the values of x it is, of course, necessary to determine at a selected temperature the pressures of a series of mixtures differing in composition. This may be done in a variety of different ways.

Firstly, there is the static method, in which the liquid remains at rest at the selected temperature and the pressure is measured by means of a manometer. This method offers no opportunity of making a chemical analysis of the vapours given off. I have used it to determine the vapour pressures of mixtures of acetone and trinitroglycerol. In this case it was necessary to conduct the experiments at a low temperature, 18° , in consequence of the instability of nitroglycerol at high temperatures. It was not possible to boil the mixtures containing little acetone on account of the very low vapour tension of the nitroglycerol. Consequently this was the most suitable method to use, but the results were somewhat disappointing in that they were not so concordant as might be desired. Fortunately they leave no doubt as to the type of the curve.

Secondly, there is Walker's method, in which a current of air is led through the liquid. This only yields accurate results when the vapour pressures are low. I have used it for the determination of the vapour pressure of pure trinitroglycerol.

The third method, namely, that of measuring the pressure under which the mixture boils at a selected temperature, has yielded excellent results in the hands of Zawidski and others. Unfortunately, it requires a considerable amount of special apparatus in order to avoid various sources of error, and even then it is difficult to maintain the temperature of the boiling liquid exactly at the correct point.

In my experiments with mixtures of water with methyl ethyl ketone and other substances which are soluble in it only to a limited extent I have made use of a fourth method, namely, that of determining the boiling point under atmospheric pressure and then calculating the vapour pressure at a selected temperature. This method has the advantage of great sensitiveness; in the case of methyl ethyl ketone and water mixtures, differences of temperature were measured which were concordant within about 0.001° , equivalent to about 0.02 mm., or about 0.003 per cent. of the total pressure. In order to be able to reduce the vapour pressures to constant temperature, it is, of course, necessary to ascertain the variation of pressure with temperature for several mixtures. It was found that an equal range of pressure corresponded to an almost equal variation of temperature in different parts of the curve. Therefore the error introduced by the correction of the pressures cannot have been great, and any small loss of absolute accuracy was more than compensated by the great relative accuracy of the observations.

Methods of Determining Partial Pressure Curves.

In order to determine these experimentally, it is necessary to distil part of a liquid mixture and analyse it. Lehfeldt and Zawidski have made use of the refractive indices to ascertain the composition of the distillate. Sometimes one of the substances is of such a nature that it can be readily determined by a chemical method. This was the case with the mixtures of diethylamine and acetone which I examined. Whatever the method employed for the analysis, it is always very difficult to obtain a sample which accurately represents the composition of the vapour given off by the liquid in the still. Zawidski's apparatus was extremely ingenious, and apparently as perfect as it was possible to make it, yet he admits that some of his results are inaccurate.

To every total pressure curve there corresponds only one possible pair of partial pressure curves, consequently it should be possible from

the total pressures to calculate the partial pressures. For this purpose, it is, however, necessary to integrate the fundamental equation (i), a problem of great difficulty. Margules has given a solution of the problem and has obtained the expressions:

$$p_1 = \pi_1 x^\alpha e^{a_1(1-x) + \frac{a_2}{2}(1-x)^2 + \frac{a_3}{3}(1-x)^3 + \dots}$$

$$p_2 = \pi_2 (1-x)^\beta e^{\beta_1 x + \frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3 + \dots}$$

where π_1 , π_2 are the vapour pressures of the pure substances. Each of these expressions involves an endless series. In order to be able to make calculations, Zawidski has restricted them to two terms each: a_1 , a_2 , and β_1 , β_2 . The equations are then, of course, only approximately accurate, but calculations based on them are still very tedious.

In my experiments on methyl ethyl ketone and water, I was particularly desirous of ascertaining the course of the partial pressure curves, but the means and time at my disposal rendered it impossible for me to carry out accurate analyses of the distillates such as those made by Zawidski. It was therefore necessary to make use of some mathematical method, but instead of integrating equation (i) by calculation, I did it by a simple graphical method. The total pressure curve having been plotted on paper, the partial pressure curves were roughly sketched in with the aid of the known data. These data were the positions and directions of the two curves at either extremity and their positions at the points corresponding to the constant boiling mixture. At convenient intervals, tangents to the curves were drawn and measured, and calculations were made to ascertain whether the measurements were in agreement with equations (v), (vi), and (viii). Where discrepancies were found, the curves were re-drawn and then re-tested, and these operations were repeated until the curves were in accord with the equations throughout their course.

In order to test this method, I have applied it to some of the mixtures investigated by Zawidski. In Table VI will be found the results obtained with mixtures of acetone and carbon disulphide. Zawidski's values for the total pressures were first plotted, and the partial pressures were obtained from them by the graphical method described. When all had been read off, they were compared with Zawidski's experimental and calculated figures. It will be seen that my results agree with Zawidski's measurements considerably better than do his own calculated results. The deviations are greatest at the ends of the curves, but as it is exactly these measurements which are most liable to experimental error, it is probable that the values for the partial pressures obtained by the graphical method are nearer to the truth than those obtained by actual experiment. The results are such as to inspire full confidence in the graphical method.

TABLE VI.

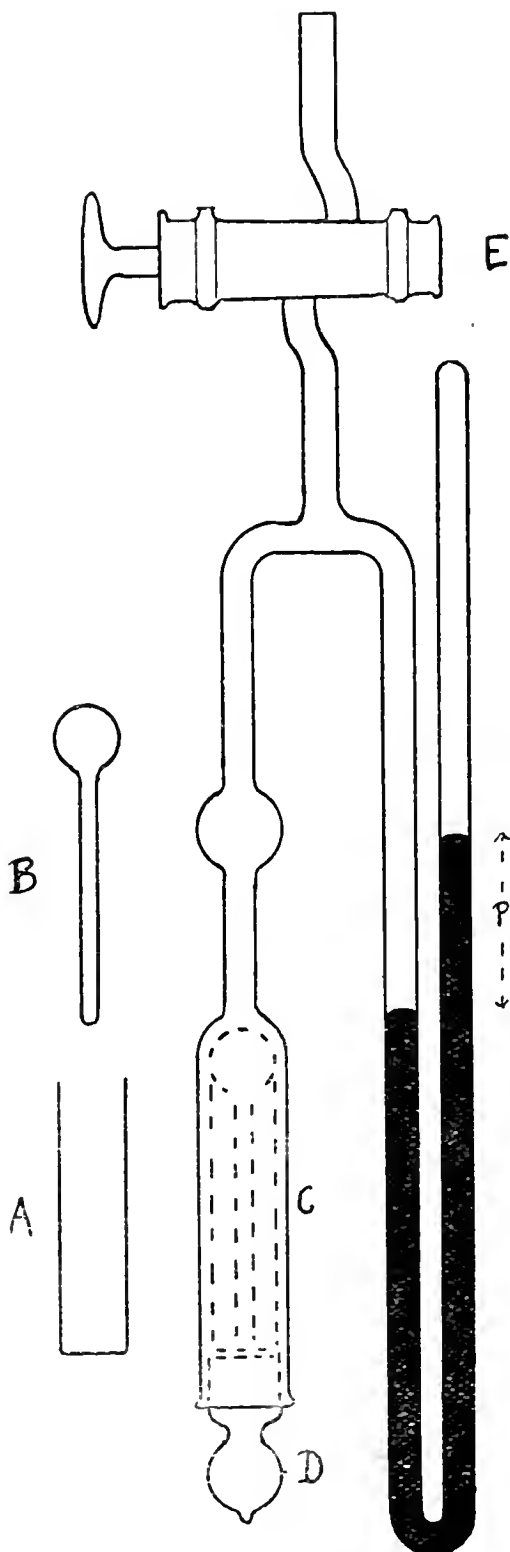
1.	2.	3.		4.		5.		6.	7.		8.	9.	10.	11.	12.
		p_1 .		p_2 .		p_3 .		Found.	p_4 .		Graph. method.	3—4.	6—7.	3—5.	6—8.
$\frac{p}{\text{Cm. Hg.}}$	p .	Found.	Calculated by Z.	Found.	Calculated by Z.	Found.	Calculated by Z.		Found.	Calculated by Z.					
0	343.8	0	—	343.8	—	343.8	—	343.8	—	—	—	—	—	—	—
0.0624	441.7	110.7	112.9	115	115	331.0	323.4	331.0	323.4	326	—	—	+7.6	-4.3	+5.0
0.0690	449.6	121.4	123.4	125	125	328.2	321.5	328.2	321.5	324	—	—	+6.7	-3.6	+4.2
0.1271	510.0	199.1	204.7	201	201	310.9	304.8	310.9	304.8	309	—	—	+6.1	-1.9	+1.9
0.1851	553.8	258.4	268.5	259	259	295.4	290.0	295.4	290.0	295	—	—	+5.4	-0.6	+0.4
0.2038	564.9	277.9	285.0	273	273	287.0	286.1	287.0	286.1	292	—	—	+0.9	+4.9	-5.0
0.2815	600.7	326.0	340.7	326	326	274.7	270.5	274.7	270.5	274	—	—	+4.2	0.0	+1.7
0.3526	622.8	359.8	374.1	360	360	263.0	259.0	263.0	259.0	262	—	—	+4.0	-0.2	+1.0
0.4100	634.6	380.8	392.8	381	381	253.7	251.5	253.7	251.5	253	—	—	+2.2	-0.2	+0.7
0.4502	641.2	392.3	402.3	395	395	248.9	246.9	248.9	246.9	246	—	—	+2.0	-2.7	+2.9
0.4953	646.1	403.6	410.3	406	406	242.4	242.5	242.4	242.5	240	—	—	-0.1	-2.4	+2.4
0.5716	652.2	419.8	420.1	421	421	232.4	236.1	232.4	236.1	230	—	—	-3.7	-1.2	+2.4
0.6144	653.7	427.6	424.6	429	429	226.1	232.7	226.1	232.7	224	—	—	-6.6	-1.4	+2.1
0.6713	655.0	437.6	430.1	439	439	217.3	227.2	217.3	227.2	216	—	—	-9.9	-1.4	+1.3
0.7208	654.6	447.2	435.7	444	444	207.4	220.5	207.4	220.5	211	—	—	-13.1	+3.2	-3.6
0.8780	645.1	464.9	453.2	460	460	180.2	191.2	180.2	191.2	185	—	—	-11.0	+4.9	-4.8
0.9116	612.2	490.3	479.0	481	481	121.8	125.4	121.8	125.4	131	—	—	-3.6	+9.3	-9.2
0.9378	598.4	492.0	484.9	484	484	106.4	106.5	106.4	106.5	115	—	—	-0.1	+8.0	-8.6
0.9584	578.1	498.5	493.2	493	493	79.6	78.1	79.6	78.1	85	—	—	+1.5	+5.5	-5.4
0.9692	564.0	502.5	497.7	499	499	62.0	60.7	62.0	60.7	65	—	—	+1.3	+3.5	-3.0
1.0	514.5	514.5	—	—	—	0	—	0	—	—	—	—	—	—	—
										Mean		±7.8	±5.3	±3.1	±3.4

Experiments with Acetone and Trinitroglycerol.

These measurements were carried out in a small glass pressure-gauge, which is shown diagrammatically in Fig. 10. Some pure nitroglycerol was first weighed into the small tube, *A*, acetone was then added and well mixed in by means of the stirrer, *B*. Then, without reweighing, *A* and *B* were introduced in the chamber, *C*, the stopper, *D*, was inserted, and the apparatus was exhausted through the cock, *E*, until the pressure of the air was reduced to a small fraction of a millimetre. The whole apparatus was then placed in a thermostat maintained at a temperature of 18° . Here it was allowed to remain with occasional tapping until equilibrium was established; usually four or five hours were required on account of the viscosity of the nitroglycerol. After the pressure had been determined, *A* and *B* were weighed and from the weight the composition of the liquid was calculated. The results are given in Table VII and Fig 11. It will be seen that the curve is of type IA.

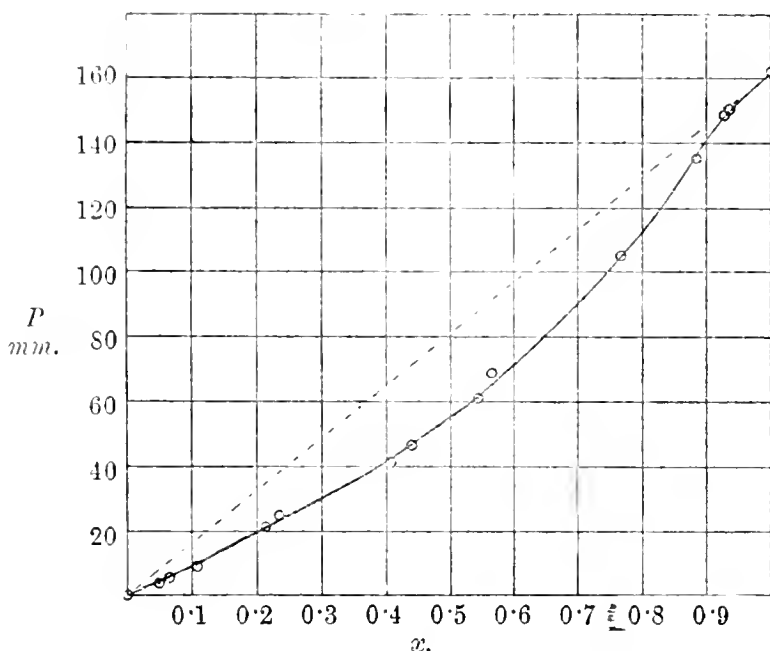
The vapour pressure of pure nitroglycerol at the temperature 18° has not been determined directly. But it has been measured at 70° by myself (see *J. Soc. Chem. Ind.*, 1904, 23, 158), and was found to be 0.051 mm. of mercury, or almost exactly equal to that of mercury itself. From this it is concluded that at 18° the vapour tension of nitroglycerol is about 0.001

FIG. 10.



mm., and is consequently quite negligible as compared with that of acetone. The total pressure curve therefore coincides with the partial pressure curve for the acetone. It was not considered advisable to conduct the experiments at a higher temperature, because nitro-glycerol has a tendency to decompose and evolve gaseous products, which would vitiate the results. The vapour pressure of the pure

FIG. 11.



acetone was found to be 162.0 mm., a figure which agrees exactly with that obtained by the extrapolation of Regnault's results.

TABLE VII.

Acetone. Per cent.	<i>w</i> .	Pressure, mm.
0	0	0.001
1.6	0.050	4.0
1.8	0.068	5.7
2.6	0.110	9.1
6.5	0.215	21.5
7.3	0.236	24.9
15.0	0.408	41.1
16.8	0.440	46.4
24.0	0.545	61.0
25.0	0.566	68.9
45.5	0.766	105.2
65.8	0.883	137.6
75.9	0.929	148.6
83.9	0.933	151.5
100.0	1	162.0

Acetone and Diethylamine.

The aliphatic amines are amongst the substances which are liable to occur in minute traces in commercial acetone (Marshall, *J. Soc. Chem. Ind.*, 1904, 23, 645). Up to the present, the only basic substances which I have succeeded in separating from this material and identifying are ammonia and methylamine, but there may be other amines of higher molecular weight present.

It seemed of interest to examine the behaviour of mixtures of acetone and some aliphatic amines, and for the first experiments diethylamine was selected, because its boiling point is almost exactly the same as that of acetone. On mixing the two liquids together, it was found that there was a fall of temperature, and it was consequently to be expected that the volume of the mixture would be greater than the sum of the volumes of the two constituents. This was found to be the case, as is shown by the following figures :

TABLE VIII.

	Acetone.	Diethylamine.
Sp. gr. 15°/15° in vacuum.....	0·79712	0·71051
Volumes taken	38 c.c.	62 c.c.
Temperature before mixing	13·3°	13·3°
" after " 		10·1°
Sp. gr. of mixture		0·74267
Volume (calculated from sp. gr.)		100·10 c.c.

The acetone had been purified by conversion into the bisulphite compound and rectification; it boiled at 56·1° under a pressure of 760 mm. The diethylamine was prepared by fractionally distilling a commercial sample. The fraction selected boiled at 55·48° to 55·49° under a pressure of 758·8 mm. This fractionation was carried out in an apparatus consisting of a column filled with glass beads and a dephlegmator, arranged similarly to the plant employed on the industrial scale for the rectification of volatile organic liquids.

Upon distillation, it was found, as anticipated, that a mixture of constant boiling point tended to come over first. After a few preliminary experiments, a mixture was made up containing about 60 per cent. of diethylamine. This was fractionated in the apparatus already described and the specific gravities of different portions of the distillate were determined. Throughout the distillation, the thermometer immersed in the vapour remained constant at 51·39° (barometer 761·5 mm.). The first 60 c.c. of distillate had the specific gravity 0·74058, a second portion 0·74070. The apparatus was then dried, and these distillates were returned to the still and again fractionated; the first portion now had the specific gravity 0·74071. To ascertain

the proportions of the two constituents which correspond to this specific gravity, different mixtures were made up and the specific gravities were ascertained. The following were the results:

TABLE IX

Percentage of diethylamine.	Sp. gr. 15°/15° in vacuum.	$\Delta\sigma$ $\Delta\pi$
π .	σ .	
59.17	0.71274	
59.63	0.71238	- 0.00078
62.05	0.71045	- 0.00080

Taking the mean of the three figures obtained from the distillates, 0.74066, the composition of the constant boiling mixture is found by interpolation to be 61.79 per cent. of diethylamine by weight or 56.21 in molecular percentages.

To ascertain whether more than one mixture of constant boiling point is formed, several different mixtures were submitted to fractionation, and the percentage of diethylamine in each distillate was determined by titration. It was found that in all cases the composition of the first portions of distillates tended towards the percentage of diethylamine already found. The total vapour pressure curve therefore evidently belongs to type IIIC. Only one mixture of constant boiling point is formed and this boils at a temperature of about 4° below the boiling points of the two constituents. This mixture contains 61.8 per cent. of diethylamine by weight or 1.28 molecules to each molecule of acetone.

Ethyl Alcohol and Methyl Ethyl Ketone.

The methyl ethyl ketone was obtained from the last runnings from the purification of commercial acetone. About a ton of this was fractionated, a portion from the middle of the distillate was dried with caustic soda, and fractionated through the bead column already mentioned; the fraction selected for the experiments boiled at 79.83° to 79.84° under 760 mm., but in spite of the constancy of the boiling point it was found afterwards to be somewhat impure; it had the sp. gr. 0.811 at 15°. The alcohol was carefully purified and rectified and had a sp. gr. of 0.794 at 15° and a boiling point of 78.3° at 760 mm. On mixing the two liquids there was a fall of temperature and a slight increase of volume. The mixture began to boil at 74.8°, and the boiling point remained constant at 75.0° (barometer, 763 mm.). Although several different mixtures were distilled, absolutely no evidence of the existence of more than one mixture of constant boiling point could be obtained. The total vapour pressure curve belongs therefore to Type IIIC.

Methyl Ethyl Ketone and Water.

The material used for this series of experiments was carefully purified; instead of being merely dried and rectified as in the last series, it was first dissolved in a 40 per cent. solution of sodium bisulphite in water, which was then kept at a temperature of about 40° for twenty hours, while air was drawn through it in order to remove any impurities which did not form non-volatile compounds with the bisulphite. The ketone was distilled off, the distillate was boiled to drive off sulphur dioxide, and then dehydrated with caustic soda or calcium chloride. The dried liquid was then submitted to fractional distillation in the bead apparatus with cooled still-head. The fraction selected boiled constantly at 79·57° under a pressure of 759·7 mm. and had the sp. gr. 0·81005 at 15°/4° in a vacuum.

Three determinations of the boiling point were then made at different times with the following results :

TABLE X.

Boiling point.	Pressure.	B. p. corrected to 760 mm.
79·57°	759·7	79·58°
79·50	758·3	79·57
79·50	758·4	79·56
	Mean.....	79·57
$\frac{\delta P}{\delta t} = 25.$		

At temperatures below 150°, methyl ethyl ketone is not miscible with water in all proportions. If a mixture which is in two layers be distilled it yields a distillate, which, although it contains both substances, is homogeneous. The behaviour of mixtures on distillation is shown by the following experiments.

A mixture of three volumes of water with two volumes of ketone when distilled through the bead apparatus gave a distillate which had the boiling point 73·38° under 755·0 mm. pressure and the sp. gr. 0·83955 at 15°/4° in a vacuum.

A second mixture which, although homogeneous, contained an excess of water gave a distillate which had the boiling point 73·38° under 755·4 mm. pressure. The sp. gr. of the first half was 0·83956, of the second half, 0·83966.

The first and last runnings of these distillates were discarded, and the middle portions were returned to the still. These gave a distillate which had the boiling point 73·72° under 764·3 mm. pressure.

A solution of ketone in water which contained only about 15 per cent. of ketone gave a distillate which had the boiling point 73·50° under

758.3 mm. pressure. The temperature remained constant at this point until almost the whole of the ketone had distilled over, then it rose suddenly to the boiling point of water.

The results of these and some other experiments are collected in Table XI.

TABLE XI.

Properties of Constant Boiling Mixture of Ketone and Water.

Boiling point.	Pressure.	B. p. corrected to 760 mm.	Sp. gr. 15°/4° in vacuum.
73.38°	755.0	73.57°	0.83955
73.38	755.4	73.56	0.83956
73.72	764.3	73.56	0.83966
73.53	758.4	73.59	0.83966
73.50	758.3	73.57	0.83966
		Mean... 73.57	Mean... 0.83962

In order to ascertain the composition of the distillate, a number of mixtures of ketone and water were made and their specific gravities were taken.

TABLE XII.

Specific Gravities of Methyl Ethyl Ketone and Water.

Water by weight. Per cent.	Sp. gr. 15°/4° in vacuum.
0	0.81005
9.826	0.83590
11.378	0.83959
11.468	0.83980

From these figures it is calculated that the mixture of constant boiling point contains

11.379 per cent. of water. $x = 0.6607$.

A mixture saturated with water at 15.0° had the sp. gr. 0.84058, and therefore contained 11.803 per cent. of water. At 15°, the solubility of water in the ketone is at a minimum, consequently there is no difficulty in obtaining a clear solution perfectly saturated at this temperature, as a rise or fall does not cause the liquid to become turbid. The solubility of the ketone in water on the contrary decreases rapidly with rise of temperature at about 15°, consequently attempts to take the specific gravity of this saturated solution were unsuccessful.

The boiling points of the pure ketone and of the heterogeneous mixture which it forms with a considerable portion of water were determined at different pressures. The results are given in Table XIII.

TABLE XIII.

Boiling Points of Ketone and of Saturated Mixtures with Water.

Pressure, mm.	Boiling temperatures.	
	Pure ketone.	Mixture with water.
760	79.54	73.62
740	78.73	72.86
720	77.91	72.09
700	77.08	71.30
680	76.24	70.49
660	75.38	69.66
640	74.50	68.80
620	73.58	67.91
600	72.63	
580	71.63	
560	70.57	
540	69.46	

Boiling-point determinations were carried out under the atmospheric pressure with a series of mixtures of the two substances in varying proportions. The determinations were made in an ordinary Beckmann apparatus. The thermometer used was the same as that employed in the former experiments: it was divided into fifths of a degree and could be read without difficulty to 0.01° .

TABLE XIV.

Boiling Points of Mixtures rich in Ketone.

Ketone. Percentage by weight.	<i>x.</i>	B. p.	Pressure.	B. p. at 760 mm.
100	1	79.50°	758.4	79.56°
99.08	0.9741	77.65		77.61
98.17	0.9306	76.36		76.42
97.28	0.8914	75.48		75.54
95.54	0.8429	74.43		74.49
93.06	0.7703	73.76		73.82
89.19	0.6736	73.58		73.64
88.45	0.6571	73.57		73.63
87.02	0.6264	73.60		73.66
85.64	0.5998	73.61		73.67
84.29	0.5730	73.61		73.67 Cloudy.

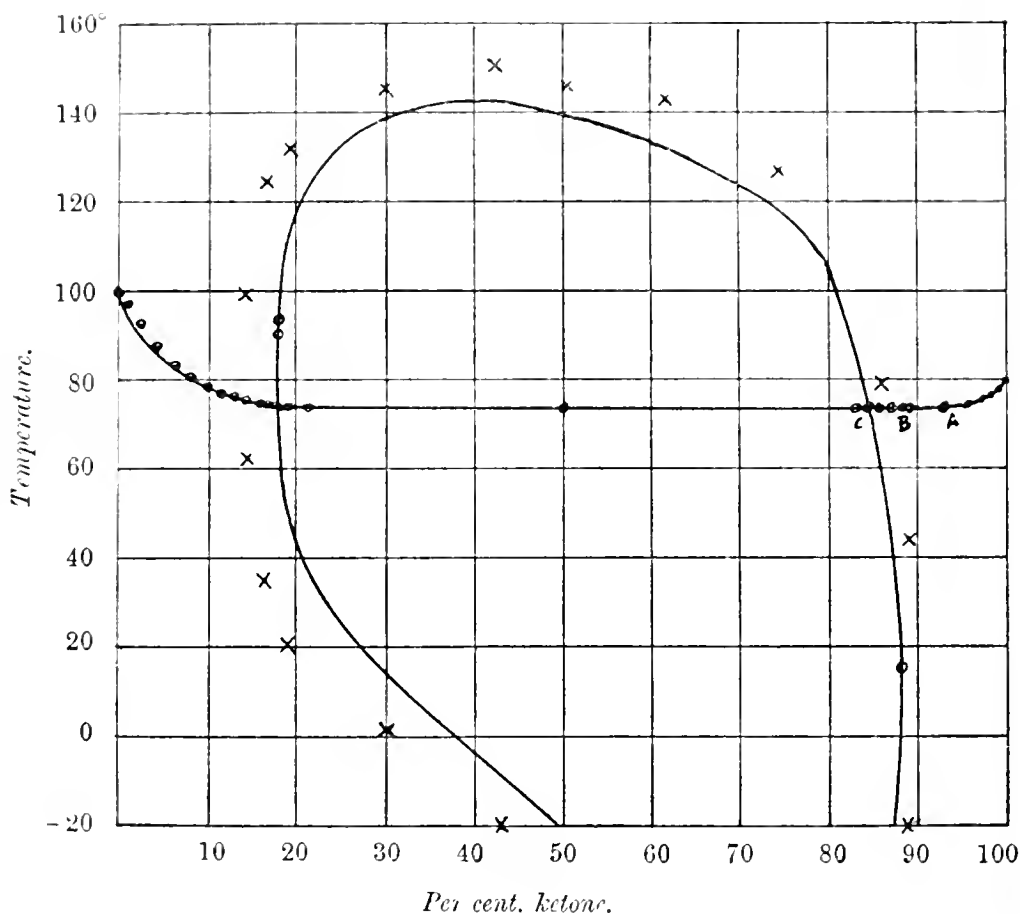
These results are plotted in Fig. 12, where they give the curve *ABC*.

It will be seen that between 93 and 84 per cent., the extreme variation was only 0.19° or about one division of the thermometer, and between 89 and 84 per cent. was only 0.04 or a fifth of a division. As these differences were too small to be observed with accuracy, the determinations were repeated with a Beckmann differential thermometer divided into hundredths of a degree.

TABLE XV.

Ketone. Percentage by weight.	n .	Thermometer reading.
89.18	0.6733	3.333°
88.07	0.6486	3.332
86.94	0.6261	3.348
85.60	0.5978	3.373
83.28	0.5546	3.387
81.03	0.5163	3.387

FIG. 12.



These results are plotted in Fig. 13 at $A'B'C'$, where the temperatures are represented on a scale many times as great as that used for the results of Table XIV. From this curve the solubility of water in ketone at the boiling point can be readily ascertained, as the curve at C' has a sharp break corresponding with the saturation point. At the temperature 73.6° a saturated solution of water in the ketone contains 14.95 per cent. of water.

A source of error which must not be lost sight of in determinations of this sort lies in the fact that the liquid mixture, when in a state of ebullition, has not quite the same composition as when originally made

up, for a portion of it is in a state of vapour or of condensate flowing back into the boiling vessel, and this portion has not the same composition as the main bulk of the liquid. But in the case of the mixtures dealt with in Tables XIV and XV the composition of the vapour is never very different from that of the liquid, and consequently this source of error may here be safely neglected.

The boiling points of mixtures containing much water and little ketone were also determined in the same manner, and are given in Table XVI.

FIG. 13.

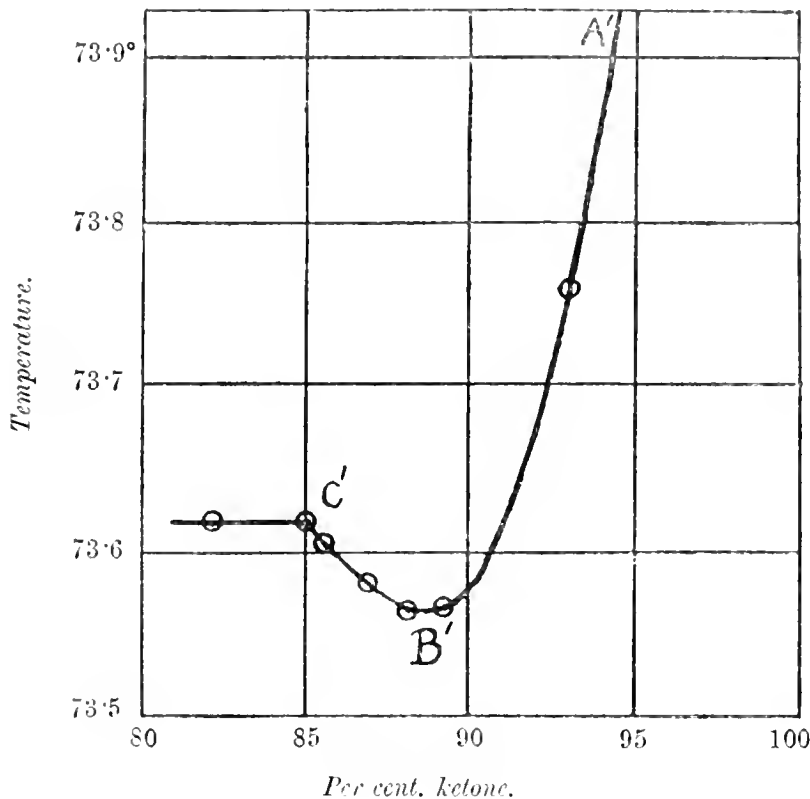


TABLE XVI.

Boiling Points of Mixtures poor in Ketone.

Ketone. Percentage by weight.	<i>x</i> .	B. p.	Pressure.	B. p. at 760 mm.
<i>First Series.</i>				
0	0	100.13	763.5	100.0°
0.4	0.001	99.3		99.2
1.2	0.003	97.3		97.2
2.7	0.007	93.1		93.0
4.6	0.012	87.4		87.3
6.4	0.017	83.3		83.2
8.2	0.022	80.8		80.7
9.9	0.026	78.8		78.7
11.5	0.031	77.2		77.1
12.9	0.035	76.2		76.1

TABLE XVI (*continued*).*Boiling Points of Mixtures poor in Ketone.*

Ketone. Percentage by weight.	<i>x</i> .	B. p.	Pressure.	B. p. at 760 mm.
<i>Second Series.</i>				
11.9	0.0324	76.64	761.2	76.47
14.0	0.0390	75.43		75.26
15.9	0.0451	74.54		74.37
15.9	0.0453	74.52		74.35
16.3	0.0461	74.40		74.23
16.6	0.0477	74.23		74.06
16.9	0.0481	74.22		74.05
17.2	0.0493	74.12		73.95
17.5	0.0504	74.03		73.86
17.8	0.0512	74.05		73.88
17.8	0.0516	74.00		73.83
18.2	0.0528	73.94		73.77 Liquid cloudy.
18.8	0.0550	73.93		73.76 "
19.6	0.0573	73.91		73.74 "
21.3	0.0630	73.91		73.74 "
50.0	0.2000	73.87		73.70 "

These boiling-point determinations were not so satisfactory as those made with mixtures containing much ketone, because the thermometer was not very steady, and the results when plotted did not fall quite on a curve of the type IV. The reason is easy to see; not only has the vapour a composition very different from that of the liquid, but it condenses into drops which do not mix readily with the bulk of the liquid in the boiling tube, and only dissolve slowly. Consequently, the boiling liquid never had the composition as made up and as given in the first and second columns of Table XVI, but always contained appreciably less ketone. The results are especially unsatisfactory when nearing the saturation point, because the condensate then dissolves very slowly in the main bulk of the liquid. Only when there is a very large excess of ketone present can the true boiling point of the heterogeneous mixture be obtained.

It is not possible therefore to determine with accuracy from the boiling-point curve the strength of the saturated solution of ketone in water. Rothmund (*Zeit. physikal. Chem.*, 1898, 26, 433) ascertained the mutual solubility of methyl ethyl ketone and water, and of other pairs of liquids, by heating together mixtures of known composition, and noting the temperatures at which dissolution was complete, or the liquid became cloudy. His results for this pair of liquids are plotted in Fig. 12, thus, \times . I have also made a few determinations by the same method in order to be able to estimate the solubility of the ketone in water at 73.6°. The mixtures examined became clear when

heated, and then at the higher temperature became cloudy again. The results, together with those obtained by me by other methods, are given in Table XVII, and are marked in Fig. 12 thus, \odot .

TABLE XVII.

Mutual Solubility of Methyl Ethyl Ketone and Water.

Temperature.	Ketone. Percentage by weight.	α .	Method.
64.7°	18.15	0.05252	Sealed tube.
65.5	18.08	0.05229	"
73.6	18.00	0.05202	Estimated.
91.0	18.08	0.05229	Sealed tube.
93.5	18.15	0.05252	"
15.0	88.20	0.6513	From sp. gr.
73.6	85.05	0.5872	From b. p. curve.

In calculating the solubility of ketone in water at 73.6°, the amount of water which separated from the 18.08 per cent. mixture at this temperature was roughly measured and allowed for.

The solubilities as measured by myself by whatever method, whether they be those of water in ketone or ketone in water, are invariably greater than those given by Rothmund. The discrepancy is probably due to the presence of impurity in the material used by Rothmund. He has himself called attention to the great influence which the presence of even a small proportion of a foreign substance may exert, but nevertheless he gives no details from which the purity of the ketone he used can be gauged, and he does not state that he submitted it to any purification.

One of the most striking features of Fig. 12 is its great resemblance to the diagrams which represent the solubilities and melting points of pairs of substances, one or both of which are fusible solids and which are partially miscible in the molten state (compare Rothmund, *loc. cit.*, p. 485; Alexéeff, *Ann. Phys. Chim.*, 1886, 28, 332). This is another instance of the analogies which exist between freezing and boiling points.

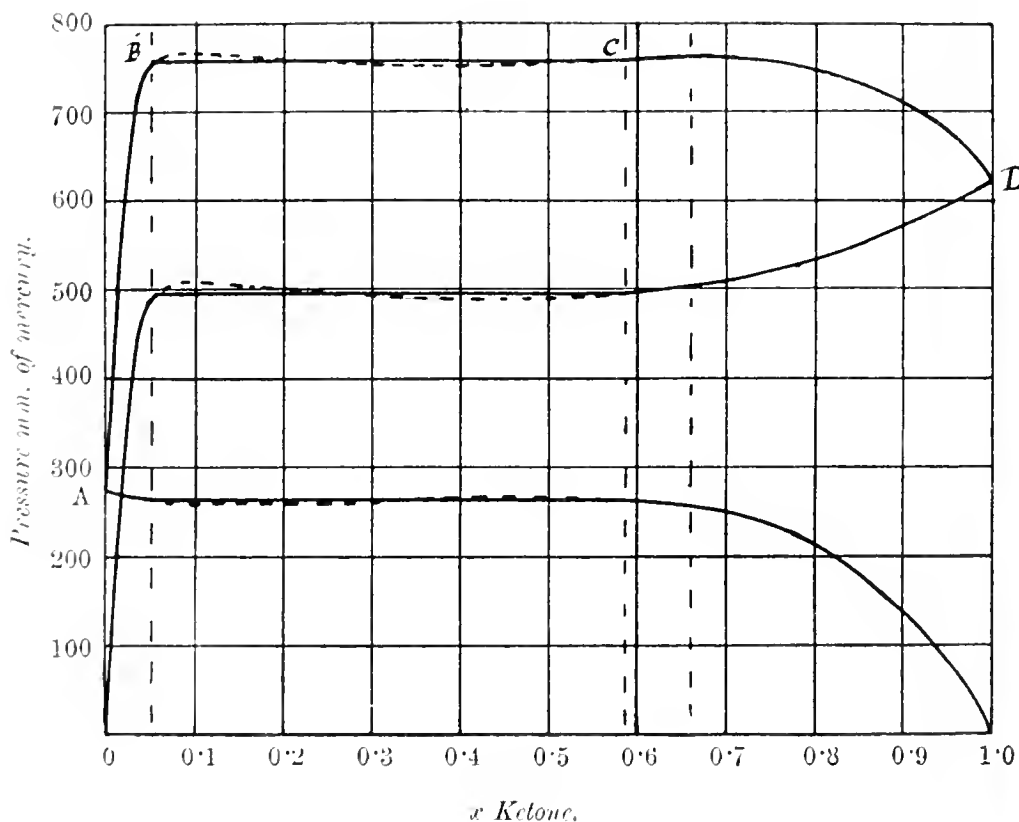
From the boiling points under constant pressure, the vapour pressures at constant temperature can be calculated by the method described above, and from the total pressures the partial pressures can be obtained by the graphical method. These operations have been carried out for the temperature 73.6°, and the results are given in Table XVIII and Fig. 14.

TABLE XVIII.

Vapour Pressures of Mixtures of Ketone and Water at 73.6°.

x .	P .	p_K .	p_W .
1.0	619.7	619.7	0
0.95	680.0	590.0	90.0
0.90	714.0	568.0	146.0
0.85	735.0	547.0	188.0
0.80	748.0	532.0	216.0
0.75	757.0	519.0	238.0
0.70	760.4	508.0	252.4
0.6606	760.9	502.7	258.2
0.65	760.9	501.6	259.3
0.60	759.8	497.0	262.8
0.5872	759.4	495.8	263.6
0.05202	759.4	495.8	263.6
0	273.0	0	273.0

FIG. 14.



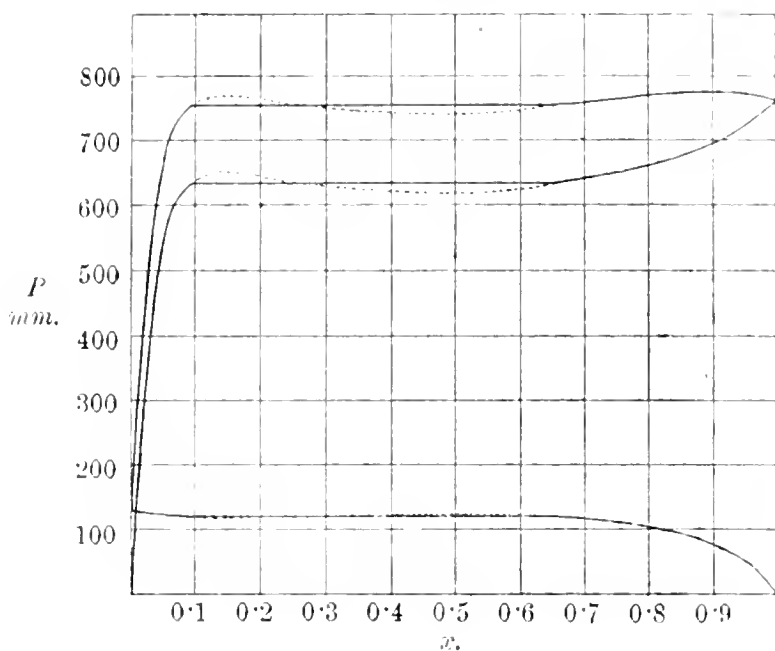
The dotted lines show the approximate course which the curves would take in the central portion, if it were possible to pass from the composition *B* to the composition *C* without the liquid separating into two layers. As a matter of fact, it always separates into two liquids,

having the compositions B , C , and consequently the vapour pressures actually found for this central portion are given by the horizontal straight lines.

Methyl Acetate and Water.

The material used for this series of experiments was not so pure as the methyl ethyl ketone employed in the last series, but the amount of impurity present was certainly very small, and insufficient to have any considerable effect on the results obtained. The experiments

FIG. 15.



were not so numerous, as their object was to ascertain the general type of the vapour pressure curves rather than to obtain complete data. The methyl acetate was purified by drying the commercial product with calcium chloride and fractionally distilling it. The fraction selected had the specific gravity 0.939 at 17° and boiled at 56.8° to 57.0° under a pressure of 758.6 mm., equivalent to 56.85° to 57.05° at 760 mm., as $\delta P/\delta t = 26.8$ mm. per degree. The results of the boiling-point determinations are given in Table XIX. The vapour pressures have been calculated from these and are plotted in Fig. 15.

TABLE XIX.

x .	B. p.	Pressure.	B. p. at 760 mm.
<i>Methyl acetate with little water.</i>			
1.0	56.93°	758.6	56.98°
0.851	56.43		56.48
0.741	56.78		56.83
0.657	57.03		57.08
0.656	57.05		57.10
0.653	57.07		57.12
0.647	57.11		57.16
0.641	57.16		57.21
0.634	57.16		57.21
0.588	57.17		57.22
0.533	57.17		57.22

Liquid cloudy.

Water with little methyl acetate.

0	99.9	757.6	100.0
0.0091	86.8		86.9
0.0179	75.8		75.9
0.0267	69.8		69.9
0.0353	65.6		65.7
0.0437	62.7		62.8
0.0520	60.65		60.74
0.0601	59.28		59.37
0.0682	58.38		58.47
0.0761	57.75		57.84
0.0838	57.39		57.48
0.0875	57.31		57.40
0.0901	57.26		57.35
0.0914	57.24		57.33
0.0930	57.23		57.32
0.0959	57.21		57.30
0.1062	57.20		57.29
0.1720	57.21		57.30

TABLE XX.

Vapour Pressures of Mixtures of Methyl Acetate and Water.

x .	P .	p_w .	p_w .
1.0	760.5	760.5	0
0.90	776	698	78
0.85	774	678	96
0.75	765	654	111
0.65	754	633	121
0.092	754	633	121
0.05	660	535	124
0	129	0	129

Ether and Water.

Only mixtures rich in ether were examined. The material was obtained by the fractional distillation of a good commercial example. The fraction selected boiled at 34.21° to 34.22° under a pressure of 755.2 mm.

TABLE XXI.

x .	B. p.	Pressure.
0	34.19°	754.5
0.106	34.01	
0.117	34.00	
0.122	34.00	
0.136	33.98	
0.144	33.98	
0.164	33.99	
0.192	33.98	
0.206	33.97	
0.222	33.95	
0.263	34.02	
0.323	34.46 (?)	
0.373	34.49 (?)	

These data not being very numerous, the partial pressures have not been calculated.

Amyl Alcohol and Water.

A few experiments were performed with mixtures of these two substances. The alcohol was not specially purified, and doubtless contained several isomerides. The figures are given here, as details of pressure curves of type IVC are almost entirely wanting.

TABLE XXII.

x .	B. p.	Pressure.
0	99.85°	756.0
0.0075	95.11	
0.0082	94.94	
0.0122	94.68	
0.0150	94.68	

Summary.

1. The curves showing the variations of partial pressure with molecular composition may be classified into four types. Of these, three relate to substances which are miscible in all proportions, and are distinguished one from the other according as p/x , the partial pressure divided by the molecular proportion, is less than, equal to, or greater than, the vapour pressure of the pure substance.

2. The corresponding total pressure curves are obtained by adding together the two partial pressure curves which are of the same type. By differentiating the equation of Duhem and Margules, it has been found possible to divide the total pressure curves into twelve types.

3. All these twelve types of total pressure curve are already known to occur, although in some cases more detailed experiments are to be desired.

4. It has been shown that with substances miscible in all proportions only one maximum or minimum can occur in the total pressure curve.

5. The rule, called by Duhem "Regnault's law," that in the case of partially miscible liquids the total pressure of the heterogeneous mixture is equal to the vapour pressure of the more volatile constituents in the pure state, has been shown to be approximately true in the case of methyl acetate and water as well as in that of ether and water, but it has also been shown that the rule is a rough approximation, and is applicable only to some cases.

6. The vapour pressures of the following pairs of liquids have been investigated experimentally: nitroglycerol and acetone, diethylamine and acetone, ethyl alcohol and methyl ethyl ketone, water and methyl ethyl ketone, water and methyl acetate, water and ether, water and amyl alcohol.

7. Methods for determining and calculating the total and partial pressures of binary mixtures have been discussed.

CXXXVI.—*A New Method for the Measurement of Hydrolysis in Aqueous Solutions, based on a Consideration of the Motion of Ions. A Correction.*

By ROBERT BECKETT DENISON and BERTRAM DILLON STEELE.

IN a recent paper (Trans., 1906, 89, 1010) the authors gave figures for the affinity constant of aniline and *ortho*- and *para*-toluidine at 18°. These numbers were calculated from data obtained for the hydrolysis constant K of the hydrochloride of the base and the dissociation constant of pure water Kw according to the relation $K = \frac{Kb}{Kw}$.

Unfortunately, through an oversight, the value of Kw for 25°, 1.2×10^{-14} , was inserted. The value of Kw , however, depends on the temperature, and at 18° is only 0.64×10^{-14} . The values for Kb at 18° thus become:

Aniline	4.0×10^{-10}
<i>para</i> -Toluidine	16.4×10^{-10}
<i>ortho</i> -Toluidine	2.95×10^{-10}

And at 25° as before :

Aniline	5.2 $\times 10^{-10}$
<i>para</i> -Toluidine	22.0 $\times 10^{-10}$
<i>ortho</i> -Toluidine	3.5 $\times 10^{-10}$

The variation in "strength" of the base with temperature is thus not so pronounced as was apparent from the numbers previously given.

We have to thank Professor Abegg, of Breslau, for kindly pointing out this error.

HERIOT-WATT COLLEGE,
EDINBURGH.

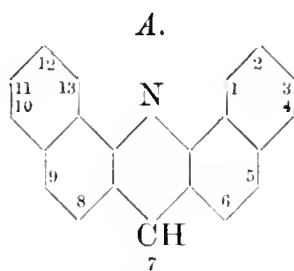
CXXXVII.—*Dinaphthacridines*.

By ALFRED SENIER and PERCY CORLETT AUSTIN.

IT may in the first place be useful briefly to review the present position of the theory of the constitution of the dinaphthacridines. As was pointed out by one of us (*Brit. Assoc. Report*, 1903, 616; *Chem. News*, 1903, 88, 272), the existence of six isomeric compounds is to be expected, and of these, four are known.

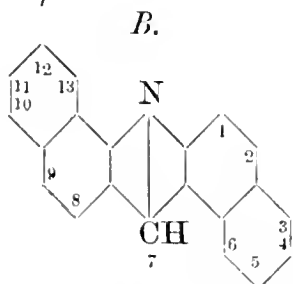
Making use of the notation proposed in the communication referred to, it will be observed that one of these is an α -N- α compound, two are α -N- β compounds, and three are β -N- β , thus :

One α -N- α :

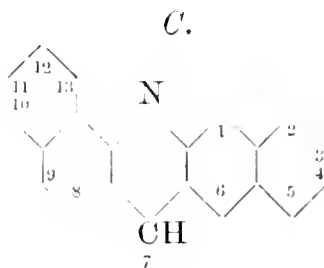


(Senier and Goodwin.)

Two α -N- β :

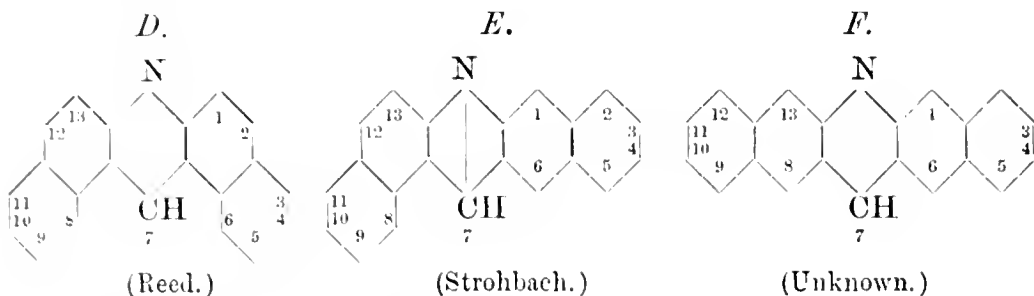


(Ullmann and Fetvadjian.)



(Unknown.)

Three β -N- β :



The behaviour of β -naphthylamine towards methylene di-iodide leads us to suppose that in the preparation of dinaphthacridines with the use of methylene compounds, the normal course of the reaction can be divided into four stages: first, condensation of the primary to a secondary amine; secondly, further condensation to a dihydro-dinaphthacridine; thirdly, oxidation to a "naphthacridine" of the type of Morgan's "*isonaphthacridine*," which we should prefer to designate as "*bisdinaphthacridine dihydride*," $[C_{21}H_{13}N]_2H_2$; lastly, oxidation to a dinaphthacridine. In our experiments with benzal chloride (phenylmethylene dichloride) and β -naphthylamine, we find that we can vary the conditions so as to obtain either the dinaphthacridine or the dinaphthylamine, and in the case of the corresponding reaction with ethylidene chloride (methylmethylene dichloride) we have not been able to get the reaction to go beyond the first stage.

That a secondary amine is first formed finds additional support in the well-known synthesis of diphenoaacridine and phenonaphthacridine from secondary amines.

α -N- α
 β -CH- β Dinaphthacridine (" *α -naphthacridine*," Senier and Goodwin)

has the structure represented by the graphic formula *A*. It is obtained by the condensation of two molecules of α -naphthylamine, forming in the first place *aa*-dinaphthylamine. Hence the dinaphthacridine must be an α -N- α compound, for which only one formula is possible.

We find that α -naphthylamine gives with benzal chloride (phenylmethylene dichloride) the corresponding 7-phenyldinaphthacridine. The constitution of the latter compound receives independent proof from the fact that we have also prepared it by the action of benzaldehyde on a mixture of α -naphthylamine and α -naphthol.

That Reed's " β -naphthacridine" is a dinaphthacridine possessing the formula *D* is also now placed beyond much doubt. Its formation from two molecules of β -naphthylamine and methylene compounds, and also by condensation of the reaction product of β -naphthol and β -naphthylamine by means of trioxymethylene (Ullmann and Fetvadjian, *Ber.*, 1903, 36, 1027), proves conclusively that the base is of the

type β -N- β . Another synthesis of the same compound by these investigators proves that one of the CH linkings is α ; for they obtain it from the reaction of 2:2-dihydroxy-1:1-dinaphthylmethane with β -naphthylamine. In this reaction one naphthol group is eliminated, which leaves the position of the C linking on that side still unproved. The nitrogen must, however, join the ring at the position of the β -hydroxyl.

That the base is symmetrical and has the formula *D*, not *E* (the only other $\begin{smallmatrix} \beta\text{-N} \\ | \\ \alpha\text{-CH} \end{smallmatrix}$ isomeride possible), may be assumed in view of, first, the analogy between its synthesis and that of the corresponding α -N- α compound; secondly, for the reasons given by Strohbach (*Ber.*, 1901, 34, 4146) in regard to the greater readiness with which substitution takes place in the α -position in the case of β -naphthylamine compounds (Möhlau and Strohbach, *Ber.*, 1900, 33, 804); thirdly, the laws put forward by Hinsberg (*Ber.*, 1902, 36, 4051), who, from a study of condensed six-membered ring compounds of carbon or of carbon and nitrogen, concludes that those which contain rings joined at an angle, *angular*, are more stable than those in which the rings are in a line, *linear*.

Strohbach's dinaphthacridine is prepared from $\beta\beta$ -dinaphthylamine-2:3-monocarboxylic acid, which shows that the condensation product derived from it must be of the type $\begin{smallmatrix} \beta\text{-N-}\beta \\ | \\ \text{CH-}\beta \end{smallmatrix}$. Its formula must therefore be *E* or *F*. *E* is chosen for the reasons stated above.

When equal weights of α -naphthylamine and β -naphthylamine are melted together and brought into reaction with methylene dichloride or methylene diiodide the resulting base is the same as the dinaphthacridine first obtained by Ullmann and Fetvadjan by the action of trioxymethylene on a mixture of α -naphthylamine and β -naphthol. That this compound has the formula *B* as stated by these chemists is settled beyond doubt, though from both the above methods of synthesis the formula *C* might also be inferred. The fact, however, that it can be obtained by the action of α -naphthylamine on 2:2-dihydroxy-1:1-dinaphthylmethane by replacement of one β -naphthol group shows that the CH group is linked on one side in the α -position and on the other side in the β -position. This excludes formula *C* and establishes formula *B*.

A fuller investigation of the $\begin{smallmatrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CH-}\beta \end{smallmatrix}$ dinaphthacridine was the object in the first instance of the experiments still to be described. It had been obtained from α -naphthylamine (2 mols.) condensed by means of methylene diiodide. This method does not give a good yield, but we are now able to suggest important improvements.

Our attempts to replace methylene diiodide by formaldehyde have

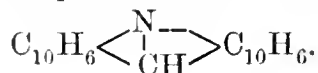
been without success, but we have found that methylene dichloride may be used to great advantage, a good yield of the base being easily obtained.

Further, using the analogous ethylidene chloride (methylmethylene dichloride) and benzal chloride (phenylmethylene dichloride), we have synthesised two new derivatives, namely, methyl dinaphthacridine $\begin{smallmatrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CMe-}\beta \end{smallmatrix}$ and phenyl dinaphthacridine $\begin{smallmatrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CPh-}\beta \end{smallmatrix}$. To these derivatives and those described previously (Senier and Goodwin) should be added the dinaphthacridine disulphonic acid discovered by Möhlau and Haase (*Ber.*, 1902, 35, 4175).

The generality of the methylene dichloride method is also shown by its application to the synthesis of the already known $\begin{smallmatrix} \alpha\text{-N-}\beta \\ | \\ \beta\text{-CH-}\alpha \end{smallmatrix}$ and $\begin{smallmatrix} \beta\text{-N-}\beta \\ | \\ \alpha\text{-CH-}\alpha \end{smallmatrix}$ dinaphthacridines and $\begin{smallmatrix} \beta\text{-N-}\beta \\ | \\ \alpha\text{-CPh-}\alpha \end{smallmatrix}$ phenyl dinaphthacridine. In the case at least of α -compounds it is by far the best method on account of the good yield and freedom from by-products. The application of the use of methylene di-iodide is extended to the synthesis of $\begin{smallmatrix} \alpha\text{-N-}\beta \\ | \\ \beta\text{-CH-}\alpha \end{smallmatrix}$ dinaphthacridine and to Morgan's "*isonaphthacridine*."

1. *Synthesis of Dinaphthacridines by the Interaction of Methylene Dichloride or its Analogues and Naphthylamines.*

1. *Methylene Dichloride and α -Naphthylamine.* $\begin{smallmatrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CH-}\beta \end{smallmatrix}$ *Dinaphthacridine* (" *α -Naphthacridine*," Senier and Goodwin),



Owing to the low boiling point of methylene dichloride (42°), the reaction cannot be carried out in an open vessel, as is the case when the di-iodide (b. p. 180°) is used. The experiments were made therefore in a closed tube heated to 220—230° for one or two hours. It was noticed that pale yellow crystals began to collect at the cooler end of the tube when the temperature of the furnace was about 210°. It was not found necessary to use pure methylene dichloride; the commercial product (Kahlbaum's "refined") was employed.

Theoretical proportions were taken, namely, α -naphthylamine (2 mols.) and methylene dichloride (1 mol.). On opening the tube a mixture of methylated spirit and a small proportion of concentrated aqueous potassium hydroxide was added and the whole heated on the water-bath for a few minutes.

The liquid was then separated from the viscous residue which contained the base and the latter was washed with cold acetone, which left the base undissolved in a crystalline form. The crystals were washed on a filter with more acetone and then with water, to remove any potassium chloride, and finally dried at 100° and recrystallised once or twice from benzene. It was rarely necessary to recrystallise further.

Dinaphthacridines are remarkable generally for their stability. They may be distilled in a partial vacuum without difficulty and, when pure, without decomposition. This process is, however, not necessary as a means of purification. In this instance the crystals melted constantly at 185.5° (189° corr.) whether distillation was employed or not. This melting point should be substituted for that previously given (Senier and Goodwin, *Trans.*, 1902, **81**, 288). The crystals are triboluminescent. Reed's base is known to possess this property (Morgan, *Chem. News*, 1905, **92**, 219; compare *Ber.*, 1904, **37**, 3697, foot-note).

0.1730 gave 0.5725 CO_2 and 0.0758 H_2O . $\text{C} = 90.25$; $\text{H} = 4.86$.

0.4117 gave 17.2 c.c. N at 10.5° and 773 mm. $\text{N} = 5.08$.

$\text{C}_{21}\text{H}_{13}\text{N}$ requires $\text{C} = 90.32$; $\text{H} = 4.66$; $\text{N} = 5.02$ per cent.

In addition to the derivatives previously described we have prepared the

Aurichloride, $\text{C}_{10}\text{H}_6 \left\langle \begin{smallmatrix} \text{N}^- \\ | \\ \text{CH} \end{smallmatrix} \right\rangle \text{C}_{10}\text{H}_6 \cdot \text{HAuCl}_4$.—This is obtained by adding a few drops of a concentrated solution of gold chloride to a solution of the base in a mixture of glacial acetic acid with a small proportion of concentrated hydrochloric acid.

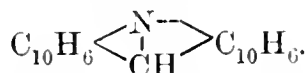
The orange precipitate is washed first with a little warm glacial acetic acid and then with dry ether. It was dried at 105° and analysed:

0.1509 gave 0.0477 Au . $\text{Au} = 31.61$.

$\text{C}_{21}\text{H}_{14}\text{NCl}_4\text{Au}$ requires $\text{Au} = 31.82$ per cent.

2. Methylene Dichloride and a Mixture of α - and β -Naphthylamines.

$\begin{smallmatrix} \alpha\text{-N} \\ | \\ \beta\text{-CH} \end{smallmatrix} \cdot \beta$ *Dinaphthacridine* (Ullmann and Fetvadjan),



When methylene dichloride (1 mol.) is heated in a closed tube with α -naphthylamine (1 mol.) and β -naphthylamine (1 mol.) at 240° for one hour, and the contents treated as in (1), yellow crystals are obtained which melt at 223° (corr. 228°). There can be no doubt that

this compound is identical with the dinaphthacridine of Ullmann and Fetvadjian (*Ber.*, 1903, 36, 1027). For the sake of comparison, however, we prepared that base according to the directions given in their paper. The two preparations were found to be identical. These chemists used α -naphthylamine and β -naphthol, but having some difficulty at first in finding the requisite temperature to bring about the reaction, we tried α -naphthol and β -naphthylamine, with the interesting result that the base was produced more readily.

This also, after frequent recrystallisation, melted constantly at the same temperature. It does not exhibit triboluminescence.

0.1916 gave 0.6329 CO_2 and 0.0837 H_2O . $\text{C} = 90.08$; $\text{H} = 4.85$.

0.3526 gave 15.5 c.c. N at 15° and 761.5 mm. $\text{N} = 5.15$.

$\text{C}_{21}\text{H}_{13}\text{N}$ requires $\text{C} = 90.32$; $\text{H} = 4.66$; $\text{N} = 5.02$ per cent.

We have prepared the following new derivatives:

Platinichloride, $[\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C}_{10}\text{H}_6]_2 \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$.—A mixture of glacial acetic acid and hydrochloric acid is generally a most convenient solvent for dinaphthacridines. This one, however, is only very slightly soluble in solvents suitable for the preparation of salts. A dilute solution was prepared in alcohol acidified with hydrochloric acid, and from this, on adding platinic chloride, a bright yellow precipitate was obtained, which, on drying in the desiccator, gave the following numbers on analysis:

0.1098 gave 0.0210 Pt . $\text{Pt} = 19.12$.

$\text{C}_{42}\text{H}_{32}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$ requires $\text{Pt} = 19.42$ per cent.

Bisdinaphthacridine hexabromide, $[\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C}_{10}\text{H}_6]_2 \text{Br}_6$, was precipitated as an orange-yellow powder when solutions of bromine and the base in chloroform were mixed. The precipitate was collected on a filter, washed with dry ether, and dried in the oven at $105\text{--}106^\circ$.

0.1014 gave 0.1090 AgBr . $\text{Br} = 45.73$.

$\text{C}_{42}\text{H}_{26}\text{N}_2\text{Br}_6$ requires $\text{Br} = 46.2$ per cent.

It is an isomeride of the two compounds previously described by us (*Trans.*, 1904, 85, 1204, 1205).

3. *Methylene Dichloride and β -Naphthylamine.* $\begin{matrix} \beta\text{-N-}\beta \\ | \\ \alpha\text{-C H-}\alpha \end{matrix}$ *Dinaphth-*
acridine (" β -Naphthacridine," Reed), $\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ | \\ \text{C H} \end{matrix} \text{C}_{10}\text{H}_6$.

Methylene dichloride (1 mol.) and β -naphthylamine (2 mols.) were heated in a closed tube at 200° for two hours and treated as above. Reed's dinaphthacridine was obtained in good yield.

4. *Ethylidene Chloride and α -Naphthylamine.* $\begin{matrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-C Me-}\beta \end{matrix}$ *Methyldi-*
naphthacridine (7-Methyl derivative of Senier and Goodwin's base),
 $\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ | \\ \text{C Me} \end{matrix} \text{C}_{10}\text{H}_6$.

Ethylidene chloride (1 mol.) and α -naphthylamine (2 mols.), heated in a closed tube at $220\text{--}230^\circ$ for two hours and treated as previously described, gave a base crystallising in distinct greenish-yellow octahedra. The action appeared to commence at 215° . The crystals melt at 219° (224° corr.) and do not exhibit triboluminescence.

0.2138 gave 0.7080 CO_2 and 0.1030 H_2O . C = 90.31 ; H = 5.35.

0.2668 ,, 11 c.c. N at 13° and 758 mm. N = 4.86.

$\text{C}_{22}\text{H}_{15}\text{N}$ requires C = 90.10 ; H = 5.12 ; N = 4.77 per cent.

The following derivatives were prepared :

Hydrochloride, $\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ | \\ \text{C Me} \end{matrix} \text{C}_{10}\text{H}_6 \cdot \text{HCl}$.—A solution of the base in a mixture of glacial acetic acid and concentrated hydrochloric acid deposited, on cooling, yellow needles. These were recrystallised from the same solvent, washed with dry ether, and dried in the desiccator. This salt is easily decomposed by water.

0.2285 gave 0.0941 AgCl . Cl = 10.17.

$\text{C}_{22}\text{H}_{16}\text{NCl}$ requires Cl = 10.77 per cent.

Aurichloride, $\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ | \\ \text{C Me} \end{matrix} \text{C}_{10}\text{H}_6 \cdot \text{HAuCl}_4$.—To a hot solution of the base, as described above for the hydrochloride, a concentrated solution of gold chloride was added. A yellow precipitate separated on cooling. It was washed with glacial acetic acid and dry ether and finally dried at 105° . It is easily decomposed by water.

0.1012 gave 0.0311 Au. Au = 30.73.

$\text{C}_{22}\text{H}_{16}\text{NCl}_4\text{Au}$ requires Au = 31.12 per cent.

Platinichloride, $\left[\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \text{---} \\ | \\ \text{C} \text{Me} \end{array} \right]_2 \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$.—A solution of platonic chloride was added to a solution of the base in alcohol, acidified with hydrochloric acid. A yellow powder was precipitated, which was washed with dry ether and dried in a desiccator. It is easily decomposed by water.

0.2085 gave 0.0396 Pt. Pt = 18.99.

$\text{C}_{44}\text{H}_{36}\text{O}_2\text{N}_2\text{Cl}_6\text{Pt}$ requires Pt = 18.89 per cent.

Dibromide, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NBr} \text{---} \\ | \\ \text{CMeBr} \end{array} \text{C}_{10}\text{H}_6$.—A solution of the base was prepared in glacial acetic acid mixed with a small proportion of toluene. To this a solution of bromine in glacial acetic acid was added. A yellow precipitate appeared, which was separated at once, washed with glacial acetic acid, then with dry ether, and dried at 105°. The compound is decomposed by water, but is somewhat soluble in glacial acetic acid or chloroform. Its solutions do not fluoresce.

0.1888 gave 0.1570 AgBr. Br = 35.38.

$\text{C}_{22}\text{H}_{15}\text{NBr}_2$ requires Br = 35.32 per cent.

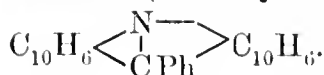
5. *Ethylidene Chloride and a Mixture of α - and β -Naphthylamines.*

Ethylidene chloride (1 mol.), α -naphthylamine (1 mol.), and β -naphthylamine (1 mol.) were heated in a closed tube at 270° for half an hour. The contents of the tube were treated in the manner previously described, when crystals were obtained identical with the base just mentioned, $\begin{array}{c} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CMe-}\beta \end{array}$ methyldinaphthacridine. No trace of the desired compound, $\begin{array}{c} \alpha\text{-N-}\beta \\ | \\ \beta\text{-CMe-}\alpha \end{array}$ dinaphthacridine, nor of any intermediate product, could be detected.

6. *Ethylidene Chloride and β -Naphthylamine.*

Ethylidene chloride (1 mol.) and β -naphthylamine (2 mols.) were heated in a closed tube at 250° for one hour. The contents of the tube were examined as before and gave crystals of $\beta\beta$ -dinaphthylamine. Heating to a higher temperature caused decomposition unless a solvent was used. We therefore added naphthalene to a fresh portion and heated it to 300°. Even in this case we only obtained $\beta\beta$ -dinaphthylamine.

7. *Benzal Chloride and α -Naphthylamine.* $\begin{matrix} \alpha\text{-N-}\alpha \\ \beta\text{-C-Ph-}\beta \end{matrix}$ *Phenyldinaphth-*
acridine (7-Phenyl derivative of Senier and Goodwin's base),



When benzal chloride and α -naphthylamine are heated together, a solid is readily formed which contains no acridine. If, however, such a solvent as naphthalene is present, the acridine is readily obtained on prolonged heating. Benzal chloride (1 mol.) is mixed with about twice its weight of naphthalene and heated to its boiling point. α -Naphthylamine (2 mols.) is then added in small portions at a time, the mixture being kept agitated and in ebullition. It is best to work with small quantities at a time in large test-tubes, when the heating can be conveniently done in the flame. The product is worked up as before and yields a yellow, crystalline powder. This on recrystallisation twice from toluene or benzene assumes the form of hexagonal plates which melt at 224° (229° corr.) and can be distilled. The crystals do not exhibit triboluminescence.

0.1750 gave 0.5853 CO_2 and 0.0776 H_2O . C = 91.21 ; H = 4.92.

0.2815 „ 9.8 c.c. N at 19.5° and 767 mm. N = 4.02.

$\text{C}_{27}\text{H}_{17}\text{N}$ requires C = 91.26 ; H = 4.79 ; N = 3.94 per cent.

We have also obtained the same compound by the application of Ullmann and Fetvadjan's method.

α -Naphthylamine (2.5 grams) was mixed with α -naphthol (3 grams) and heated to boiling. Excess of benzaldehyde was used, only a few drops at a time being added. Heating was continued for some time. On cooling, the mass was boiled with a little toluene, filtered, and the residue recrystallised from more toluene. The resulting substance was identical with that just described.

The following derivatives were prepared :

Hydrochloride, $\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ | \\ \text{C-Ph} \end{matrix} \text{C}_{10}\text{H}_6, \text{HCl}$.—Yellow crystals of this salt were obtained by dissolving the base in a hot mixture of glacial acetic acid and concentrated hydrochloric acid and allowing the solution to cool. These were recrystallised from the same solvent, washed with dry ether, and dried in a desiccator.

0.3415 gave 0.1312 AgCl . Cl = 9.49.

$\text{C}_{27}\text{H}_{18}\text{NCl}$ requires Cl = 9.06 per cent.

The specimen was evidently not quite pure.

Platinichloride, $\left[\text{C}_{10}\text{H}_6 \begin{matrix} \text{N} \\ | \\ \text{C-Ph} \end{matrix} \text{C}_{10}\text{H}_6 \right]_2, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$.—To the

last-mentioned solution of the base, platinum chloride was added, when an orange precipitate was obtained. This was washed successively with glacial acetic acid and dry ether and dried in a desiccator.

0.0944 gave 0.0160 Pt. Pt = 16.94.

$C_{54}H_{40}O_2N_2Cl_6Pt$ requires Pt = 16.86 per cent.

Aurichloride, $C_{10}H_6 \begin{smallmatrix} N \\ | \\ CPh \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \diagup \diagdown \end{smallmatrix} C_{10}H_6, HAuCl_4$.—This was prepared from gold chloride in a manner similar to that used for the platinum chloride. It is a yellow, crystalline powder.

0.1445 gave 0.0406 Au. Au = 28.09.

$C_{27}H_{18}NCl_4Au$ requires Au = 28.34 per cent.

8. Benzal Chloride and a Mixture of α - and β -Naphthylamines.

It was hoped by this reaction to prepare the already known α -N- β -CPh- α phenyldinaphthacridine (Ullmann and Fetvadjian, *Ber.*, 1903, **36**, 1029), but so far the experiment has not yielded a definite result.

9. Benzal Chloride and β -Naphthylamine. β -N- β -CPh- α Phenyldinaphthacridine (7-Phenyl derivative of Reed's base), $C_{10}H_6 \begin{smallmatrix} N \\ | \\ CPh \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \diagup \diagdown \end{smallmatrix} C_{10}H_6$.

This reaction requires special care, as secondary products are easily formed.

If the two reagents are heated alone, the resulting compound is $\beta\beta$ -dinaphthylamine. Generally the method followed for the preparation of the dinaphthacridine was the same as in the corresponding experiment with α -naphthylamine. The benzal chloride and naphthalene were first heated together to boiling, then the β -naphthylamine was added in small portions at a time in order to avoid loss by distillation. A solid separated which contained the acridine. On partial cooling, the liquid was decanted from the solid and again heated, when more of the solid separated. This process was repeated until no more solid could be obtained. The solid product was then worked up in the usual way. It was recrystallised from benzene or toluene, when it assumed the form of pale yellow needles melting at 293° (301.5° corr.). It is identical with the compound described as *meso*-phenyl- β -naphthacridine by Claus and Richter (*Ber.*, 1884, **17**, 1595). It has also been investigated by Ris (*Ber.*, 1884, **17**, 2030), Klopsch (*Ber.*, 1885, **18**, 1586), Haase (*Ber.*, 1903, **36**, 592), and Ullmann and

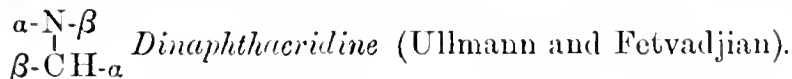
Fetvadjian (*loc. cit.*). It is more soluble in glacial acetic acid than in toluene, very soluble in chloroform or carbon disulphide, and insoluble in ethyl acetate. It is less soluble than the α -isomeride in benzene and toluene.

II. Further Study of Dinaphthacridines. Synthesis by the Interaction of Methylene Di-iodide and Naphthylamines.

1. Methylene Di-iodide and α -Naphthylamine. $\begin{matrix} \alpha\text{-N-}\alpha \\ | \\ \beta\text{-CH-}\beta \end{matrix}$ Dinaphthacridine (Senier and Goodwin).

The method by which this compound was originally prepared gives only a small yield. If the alkali be omitted the action is too energetic, even when small quantities are used, and loss by decomposition is the result. Solvents were then tried, including benzene, naphthalene, paraffin wax, and benzoic acid. The last mentioned gave very satisfactory results. The α -naphthylamine was mixed with about twice its weight of benzoic acid, the methylene di-iodide added, and heat applied in the usual way. Before recrystallising, the contents were heated to boiling with a mixture of methylated spirit and a small proportion of concentrated aqueous potassium hydroxide. This treatment removes hydrogen iodide and benzoic acid.

2. Methylene Di-iodide and a Mixture of α - and β -Naphthylamines.



This method seems to be very satisfactory for the preparation of this base. It is, however, necessary to use alkali.

Methylene di-iodide (1 mol.) is mixed with α -naphthylamine (1 mol.), β -naphthylamine (1 mol.), and an excess of previously ignited potassium carbonate (3 mols.). The mixture is either heated in a closed tube at 200° for two to four hours, or heated to 200° in an open flask with a reflux condenser for the same length of time.

The product is boiled with a mixture of toluene and absolute alcohol and the hot solution filtered from potassium salts. On cooling, the solution deposits yellow crystals, which, on recrystallisation from toluene, melt at 223° (228° corr.). This compound is identical with

the $\begin{matrix} \alpha\text{-N-}\beta \\ | \\ \beta\text{-CH-}\alpha \end{matrix}$ dinaphthacridine described in this paper. In some experiments the alkali was omitted, but it was then found more difficult to prevent over-heating.

3. *Methylene Di-iodide and β -Naphthylamine.* $\begin{matrix} \beta\text{-N-}\beta \\ \alpha\text{-CH-}\alpha \end{matrix}$ *Dinaphth-*
acridine (Reed) and *Bisdinaphthacridine Dihydride* [*isoNaphth-*
acridine," Morgan], $(\text{C}_{21}\text{H}_{13}\text{N})_2\text{H}_2$.

When methylene di-iodide (1 mol.) and β -naphthylamine (2 mols.) are mixed with excess of potassium carbonate in an open vessel and treated in the usual way, or when the alkali is omitted, Reed's dinaphthacridine is obtained and no trace of Morgan's base is formed. If, however, potassium hydroxide, previously fused and powdered, replaces the carbonate, only orange crystals are obtained, which are identical with bisdinaphthacridine dihydride (*isoNaphthacridine*," Morgan, *Trans.*, 1898, **73**, 536; *Naphthacrihydridine*," Möhlau and Haase, *Ber.*, 1902, **35**, 4169). In a closed tube with potassium carbonate, a mixture of the two bases is obtained, Morgan's predominating.

In the above investigation we repeated the experiments of Ullmann and Fetvadjan to obtain Reed's base from β -naphthylamine, β -naphthol, and trioxymethylene, and found that Morgan's base was first formed as an intermediate product. It was, indeed, the chief product of the reaction when the temperature did not exceed 225° , whereas at 250° Reed's base predominated. That the orange crystals obtained by the above methods are really crystals of the substance obtained by Morgan and reinvestigated by Möhlau there can be no doubt, although the melting point was found to be 243° (248° corr.), whereas Morgan gives 227° and Möhlau 236° . The compound is easily distinguished from Reed's dinaphthacridine by its higher melting point and characteristic colour, and the two substances may be easily separated by fractional crystallisation from toluene, when the less soluble orange compound is first deposited in long needles, the dinaphthacridine forming more compact greenish-yellow crystals when the mother liquor has been evaporated to a small bulk. To remove any possible doubt as to the identity of the orange crystals with Morgan's base, we first converted it into the characteristic green hydrochloride (by passing hydrochloric acid gas into a benzene solution of the base). The green salt of Morgan's base gradually changed to the yellow salt of Reed's base (compare Morgan, Möhlau and Haase, *ibid.*), and from the latter Reed's base was obtained; secondly, we oxidised the compound by well-known methods, with bromine, also with nitrous acid, and in both cases obtained Reed's base; thirdly, the latter was reduced by sodium amalgam to orange crystals melting at 243° (248° corr.); fourthly, we submitted the compound to analysis:

0.2795 gave 0.9224 CO_2 and 0.1284 H_2O . $\text{C} = 90.00$; $\text{H} = 5.10$.

0.3093 „ 13.4 c.c. N at 19° and 765 mm. $\text{N} = 5.01$.

$\text{C}_{42}\text{H}_{28}\text{N}_2$ requires $\text{C} = 90.00$; $\text{H} = 5.00$; $\text{N} = 5.00$ per cent.

For the earliest experiments on the synthesis of the $\begin{smallmatrix} \alpha\text{-N} & \beta \\ & \beta\text{-CH-}\alpha \end{smallmatrix}$ dinaphthacridine by using methylene di-iodide we are indebted to Miss F. M. G. Micklethwait.

QUEEN'S COLLEGE,
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CXXXVIII.—*The Interaction of Chlorine and Hydrogen.*

By CHARLES HUTCHENS BURGESS and DAVID LEONARD CHAPMAN.

THE well-known fact that hydrogen and chlorine combine under the influence of light was first observed by William Cruickshank (*Nicholson's Journ.*, 1801, [i], 5, 202), who also noticed that the volume of a mixture of these gases over chlorine water did not begin to diminish until the light had exerted its influence for several seconds. Cruickshank's observation was confirmed by Dalton (*A New System of Chemical Philosophy*, p. 300).* Draper (*Phil. Mag.*, 1844, [iii], 25, 9, and 1845, [iii], 26, 473) by several conclusive experiments established the fact that no hydrochloric acid is formed in a freshly-prepared mixture of chlorine and hydrogen until the gases have been subjected to the influence of light for a measurable period of time, but that after interaction starts the rate of formation of hydrogen chloride increases and ultimately becomes constant. A period of comparative inactivity in the initial stage of a chemical change has been called by Bunsen and Roscoe an induction period. The induction period which accompanies the interaction of chlorine and hydrogen in light is the most familiar example of the phenomenon. Since the time of Draper it has been studied by various authors, mostly with a view to elucidating the actual mechanism of the chemical change. The hypotheses which have been the direct outcome of these investigations can be roughly grouped under three heads, namely :

(1) Draper's theory : that light increases in some unknown way the

* The history of photochemistry is dealt with very completely in J. M. Eder's *Handb. der Photographie*, 1884, I ; in Ostwald's *Allgemeine Chemie*, II, 396—458 ; and, in relation to chlorine, in J. W. Mellor's paper (*Trans.*, 1901, 79, 216).

electro-negative properties of chlorine, and thereby exalts the affinity between chlorine and hydrogen.

(2) Bunsen and Roscoe's theory: that light gradually removes the resistance which opposes the force of affinity.

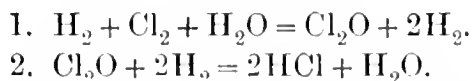
(3) The intermediate compound theories: that chlorine and hydrogen cannot directly interact, but that the observed change is actually the sum of several distinct chemical transformations.

In support of his hypothesis Draper states that chlorine which has been submitted to the action of light for a sufficient length of time acquires the property of instantly combining with hydrogen under the influence of light, and that therefore the element chlorine can pass gradually from an inactive to an active state. According to this authority the agency which effects the change is tithonicity, an essential constituent of sunlight. It is absorbed and retained by chlorine, the affinity of that element for hydrogen being at the same time increased. The following simple deduction from this hypothesis is contradicted by experience. The electro-negative properties of chlorine which had been exposed to light for a sufficient length of time would be increased to such an extent that a mixture of the gas with hydrogen would exhibit temporarily an abnormal sensitiveness to the influence of light, and might even be partially transformed into hydrogen chloride in the dark. Apparently Draper made no attempt to test this point.

Bunsen and Roscoe were unable to confirm Draper's statement that chlorine which had been prepared and kept in the dark and chlorine which had been exposed to light differed in their behaviour towards hydrogen. Objection was therefore taken to the view, that of the two gases chlorine alone was changed during the induction period. According to them the circumstance that chlorine and hydrogen could be intimately mixed without combination taking place was to be explained by there being in that case a resistance which opposed the force of affinity, whilst the fact that light transformed the mixture into hydrogen chloride was to be regarded as due to the removal of this resistance by the light. On standing in the dark, an insulated mixture was found to return after a time to its former inactive condition, so that a spontaneous development of the force which opposed the chemical affinity of the elements had to be regarded as an inherent characteristic of the mixture. It does not appear to have been noticed hitherto that if such were the case, the velocity of chemical change could not at any time be exactly proportional to the intensity of illumination, since light below a definite, although small, intensity would be unable to prevent the mixture from returning to an inactive state.

In all the theories based on the assumption of an intermediate com-

pound, water molecules have played an essential part. According to Pringsheim (*Wied. Ann.*, 1887, 32, 384), the successive changes are possibly embodied in the following equations :



Mellor has shown, however, that the actual addition of either hypochlorous acid or chlorine monoxide to the system does not shorten the time of induction. Accordingly he assumes that if an intermediate compound is formed at all, it must be a complex molecule of the type $\text{Cl}_{2x}(\text{H}_2\text{O})_y\text{H}_{2z}$. Hydrogen was introduced into the formula of this compound on account of Bunsen and Roscoe's statement that the properties of moist chlorine are not changed by the exposure of the gas to light.

Bevan found that the foregoing statement of Bunsen and Roscoe was not correct, that Draper was in fact right in stating that moist chlorine is actually changed by light, and that Bunsen and Roscoe's inability to confirm Draper's result was due to the circumstance that in the experiment of the former the insulated chlorine before being tested was bubbled through water, in the presence of which liquid the acquired characteristics of the gas were shown by Bevan to be destroyed. This discovery, coupled with the fact that the least expansion capable of producing a cloud in chlorine saturated with water vapour is less in the illuminated than in the darkened gas, caused Bevan to infer that the first action of the light on a moist mixture of chlorine and hydrogen was to produce an addition compound of chlorine and water, the molecules of which could act as condensation nuclei for water vapour. He further assumed that the compound of chlorine and water would, after it had combined with hydrogen, break up into hydrogen chloride and water.

With the facts before us three objections can be urged against the theory of an intermediate compound. Firstly, in order to account for an induction period of measurable length an appreciable quantity of the intermediate compound must be formed. The compound should therefore be capable of being isolated. Secondly, the theory does not afford an explanation of the fact observed by Draper, namely, that for some time after the electrolytic gas has been exposed to light there is no hydrogen chloride produced.* Finally, as Dyson and Harden (*Trans.*, 1903, 83, 29) have pointed out, it will not account for the induction period which is observed with an almost dry mixture of carbon monoxide and chlorine. The latter investigators suggest that it is possible that the light brings about the formation of a compound which acts as a carrier for one of the interacting gases.

* This fact was not confirmed by Mellor or Bevan.

It must here be mentioned that van't Hoff denies that an induction period is a real and general characteristic of a simple chemical change. Its existence is, according to him, merely an indication that some necessary precaution has been omitted. This anticipation we have found in the present case to be correct. The observed delay in the combination of chlorine and hydrogen is due to the circumstance that the gases contain impurities which are capable of preventing the formation of hydrogen chloride, and are themselves gradually destroyed in the light. In the course of our work, after the existing theories had been further tested and found unsatisfactory, we were led to suspect that the above was the right explanation. As soon as this

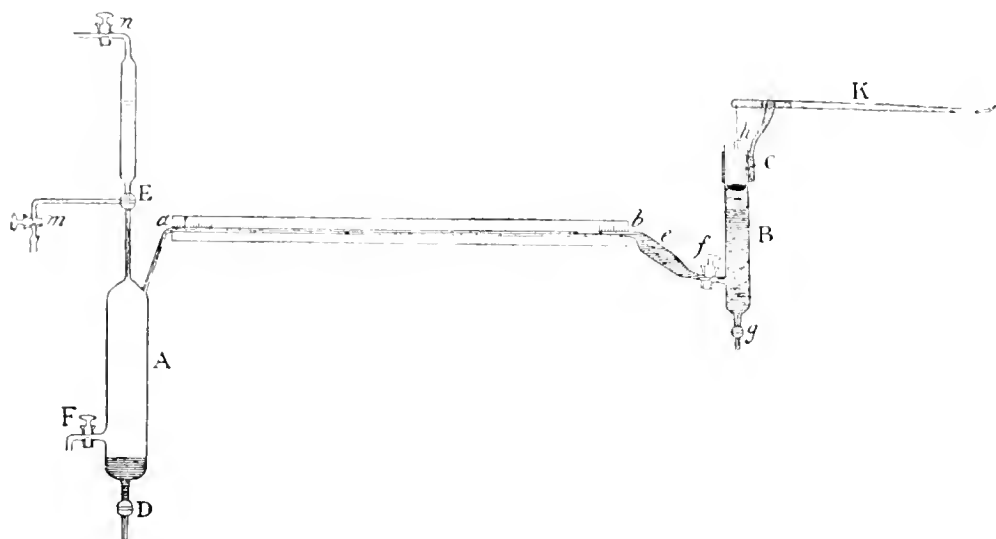


FIG. 1.

was realised, little difficulty was experienced in finding the effective impurities, and in accounting for many of the previously observed facts.

EXPERIMENTAL.

The mixture of chlorine and hydrogen was prepared by the method recommended by Bunsen and Roscoe, namely, by the electrolysis of a strong aqueous solution of hydrogen chloride.

Several forms of actinometer, which were all similar in principle to that used by Bunsen and Roscoe, were employed. For most purposes the apparatus shown in Fig. 1 was found to be the most convenient. The insolation vessel, *A*, was a wide glass tube and its total capacity was about 70 c.c. This vessel communicated with a capillary tube, *ab*, to which a scale was attached. The end, *b*, of the capillary tube was fused to a wider and slightly inclined tube, *e*, which was separated from the wide vertical tube *B* by the tap *f*. Water could be drawn into *B* through the tap *g*. As a rule the required information about

the rate of formation of hydrogen chloride was obtained by direct observations being made on the movement of the thread of water along the capillary tube *ba*, but in some cases this was found to be too tedious owing to the extreme length of the induction period. Accordingly when it was thought that an exposure to light of several hours would be necessary, an automatic method of recording the result was resorted to. This was accomplished by a simple addition to the apparatus. A glass float, *C'*, consisting of a glass tube closed at the bottom and drawn out to a narrow hooked tube, *h*, at the top, was ground so as to fit *B* loosely. A lever, *k*, was firmly clamped to the tube *B*. The end of the lever immediately above the float was attached to the small tube *h* by a silk thread which was fixed at both ends with sealing wax. The other end of the lever marked with a pointer, cut out of a sheet of aluminium foil, on a revolving drum, which had previously been covered with smoked paper. Above the insolation vessel and communicating with it by a three-way tap was a graduated tube which was used to add measured quantities of liquid to the actinometer. On to the bottom of the insolation vessel a capillary tap, *D*, was fused. The actinometer was filled in the following manner. The insolation vessel, the capillary tube *ab*, and the index reservoir *B* were first completely filled with water. The mixed gases from the electrolytic vessel were then led by way of the taps *m*, *E*, and *n* through the graduated tube for several hours. The gases after passing through *n* were led into potash in order to absorb the chlorine. As soon as it was thought that the gas coming from the cell was sufficiently sensitive, the tap *E* was turned so that the current of gas passed into the insolation vessel. The liquid in the index tube was displaced by gas and the current was maintained in the same direction until the water in *B* had been saturated with chlorine. The tap *f* was then closed, and *D* opened and the water in *A* expelled. During this part of the operation some chlorine is absorbed by the water, and accordingly if it was desired to fill the insolation vessel with a mixture of the same composition as that coming from the cell, the gas had to be passed through the insolation vessel for some time after all the water had been displaced.

When the actinometer has been filled with gas, a measured quantity of liquid can be introduced from the graduated tube above the insolation vessel. The liquid thus introduced, of course, disturbs the composition of the mixture and reduces its sensitiveness to light; the maximum sensitiveness can, however, be easily restored by passing a current of electrolytic gas through the insolation vessel from *E* to *F*. During an experiment the insolation vessel was immersed in a water tank with parallel glass sides, the water being as a rule maintained at a constant temperature. The source of light was either an electric

lamp or a Harcourt pentane lamp. A variety of different forms of actinometer have been used for different purposes; most of the variations can, however, be readily described by reference to the above typical form.

When an actinometer containing electrolytic gas and ordinary tap water is exposed to light, the index remains practically stationary for some time. As a rule there is at first a slight expansion of the gas in the insolation vessel, but whenever the temperature of the water in the tank is kept constant it is not observed. This slow preliminary expansion, which was first observed by Draper, is therefore only the result of a slight rise in temperature of the surroundings, due to the heat emitted by the source of light. If during the first part of the induction period the lamp is shaded, no contraction is noticeable, and on re-exposure of the insolation vessel to light there is no sudden expansion. To all appearance, therefore, electrolytic gas can be subjected under certain conditions to the action of white light of moderate intensity without undergoing any change which is accompanied by a permanent or temporary alteration in the volume of the mixture. A change is, however, gradually taking place, for on the illumination being continued it is noticed after some time that the index begins to move at first very slowly and then more rapidly towards the insolation vessel.

The rate of movement soon attains a maximum. It then falls a little and finally becomes constant. The following example will suffice as an illustration. The light was a 25 c.p. Swan lamp placed at a distance of 90 cm. from the insolation vessel, which was immersed in the glass tank filled with water at the temperature of the laboratory.

Time.	Reading in cm.	Rate of movement.
11.43	1.50	—
11.45	1.45	-0.05
11.47	1.40	-0.05
11.49	1.30	-0.10
11.51	1.25	-0.05
11.53	1.20	-0.05
11.55	1.25	0.05
11.57	1.25	0.00
11.59	1.30	0.05
12.1	1.50	0.20
12.3	1.75	0.25
12.5	2.10	0.35
12.7	4.80	2.70
12.9	19.30	14.50
12.10	26.20	13.80
12.11	32.90	13.40
12.12	39.40	13.00
12.13	45.50	12.20
12.14	51.70	12.40
12.15	57.85	12.30

It will be observed that the rate of movement of the index attained its maximum value just after the period of induction.

When the exposure has been continued so long that the velocity of movement of the index has become constant, the Draper or Pringsheim effect, as it is sometimes called, can be observed. We have already stated that this effect cannot be obtained when the gases in the insolation vessel are inactive.* Therefore, it is probably due to the heat disengaged during the formation of hydrogen chloride, a conjecture which is also supported by the fact that the magnitude of the effect is roughly proportional to the sensitiveness of the mixture used in obtaining it. Both Mellor and Bevan arrived at the same conclusion.

During the final stage of the induction period, when hydrogen chloride begins to be formed, the inner surface of the glass insolation vessel becomes dim owing to the condensation upon it of a strong aqueous solution of hydrogen chloride. The strong acid is a good solvent for chlorine, and therefore some of the latter gas is carried into solution. It is probably for this reason that the index moves at its maximum rate just after the induction period is over. That chlorine is actually dissolved in the hydrochloric acid produced can be easily demonstrated by the backward movement of the index which results from shaking an insolation vessel in which hydrogen chloride has just been formed by the action of light. The index of an actinometer containing recently formed hydrogen chloride is also gradually driven back by the disengaged chlorine when the instrument is simply allowed to stand in the dark.

Another result of shaking an actinometer which has been exposed to light until the indications of the instrument have become constant is that the electrolytic gas again becomes inactive. For on the insolation vessel being exposed again to light, the first period of illumination is one of induction. The electrolytic gas can be insolated and rendered inactive again by being shaken with the liquid several times in succession, but each time that this is done the induction period is of less duration than the preceding one, and when the foregoing operations have been repeated many times, no further indications of an induction period can be observed. The following results of an actual experiment will suffice as an illustration :

The duration of the successive induction periods in minutes were given by the numbers 26, 14, 10, 8, 6, 4, 4, 4, 2, and after the operations described above had been repeated many more times it was found that the gas could not be rendered inactive again by shaking it with the liquid.

* Throughout this paper the adjective "inactive" is used to describe the condition of chlorine which has not been insolated.

This experiment demonstrates that the aqueous chlorine solution in the actinometer possesses (although only to a limited extent) the property of absorbing or destroying the activity of the insolated gas, so that in every future experiment full consideration must be given to the condition of the liquid as well as to that of the gas contained within the insolation vessel. Water which has lost the property of destroying or removing the activity of electrolytic gas will be subsequently described as active.

Whilst the above experiments were being performed, the following interesting observation was made. When an actinometer which contained active electrolytic gas and active liquid was shaken vigorously and then suddenly exposed to light, the Draper expansion was almost twice as great as that observed when the actinometer had not been agitated previously, the other conditions having been the same. In the former case, the illumination of the mixed gases was accompanied also by the formation of a cloud which rapidly subsided, but no cloud made its appearance if the liquid had not been shaken vigorously immediately before the insolation vessel was exposed to light. The reason for the observed difference was that the shaking of the liquid caused a number of minute drops to be formed. On these, hydrochloric acid condensed when the actinometer was illuminated, but in the case of no drops having been present the whole of the hydrochloric acid produced was condensed on the walls of the vessel. In the first case, the sensible heat developed by the condensation of hydrochloric acid would be communicated to the gas and assist in raising its temperature, whereas, in the second case, it would be rapidly conducted through the walls of the containing vessel. So that the fact that the Draper effect can be enhanced under the above-mentioned conditions is readily accounted for without it being necessary to assume that the greater expansion is accompanied by the formation of a greater amount of hydrogen chloride.

We have just seen that the state of activity of the liquid as well as of the gaseous contents of an actinometer must be regarded as capable of variation. On this account it became necessary that several points should be re-examined, fuller consideration being given to the condition of the liquid than had hitherto been the case. The first difficulty to be investigated was the obvious discrepancy between Bunsen and Roscoe's statement, that the resistance to combination which is removed by the action of light is gradually restored when the mixture of chlorine and hydrogen is allowed to stand in the dark, and the law of photochemistry which asserts that the amount of chemical change is proportional to the intensity of the light. Could the decay in activity noticed by Bunsen and Roscoe and by all subsequent observers be due to the circumstance that the whole of the liquid had not been rendered

completely active before the attempt to measure the rate of decay was made? An experiment was undertaken to test the accuracy of this conjecture, but it was found that even when the utmost precautions were taken to make the whole of the liquid contained in the actinometer completely active a gradual decay of activity similar to that described by Bunsen and Roscoe actually took place. The reason for this result was not discovered until much later.

We next turned our attention to two other points in the investigation of which by previous workers there appeared to be some reason for thinking that the precaution just mentioned had not been carefully observed. In the first place, several experiments demonstrated satisfactorily that hydrogen would instantly interact with previously insolated chlorine in the light, but we were forced to conclude, after several unsuccessful attempts to prove the reverse had been made, that it is impossible to raise the activity of chlorine by insolation to such an extent that on its being mixed with hydrogen and exposed to light a period of *deduction* or fall in the rate of interaction with hydrogen can be observed. In other words, the activity of chlorine separately insolated never exceeds that of chlorine insolated in the presence of hydrogen. In the second place it was established that in a mixture containing equal volumes of active and inactive electrolytic gas no hydrogen chloride was formed during the first few minutes of the illumination. It would appear to be impossible to reconcile the first result with Draper's hypothesis, or either of the two results with any intermediate-compound hypothesis which up to the present has been suggested as an explanation of the period of induction. The facts seem to point to the conclusion that there is some principle which can act like a resistance to combination, that the principle can be destroyed by light, and that it is contained in freshly-prepared chlorine and in ordinary water, but not in hydrogen. The objection to regarding the resistance in question as anything material is the fact that it can be restored to electrolytic gas from which it has been completely removed by allowing the mixed gases to stand in the dark.

We will now give without details the results of a series of comparative experiments performed with two similar actinometers. Working with these actinometers we were able to compare the state of activity of two specimens either of gas or of liquid which differed as a result of the treatment to which they previously had been subjected. During the time that measurements were being made the insolation vessels of both actinometers were placed in a glass tank filled with water and were disposed in such a manner that they could be illuminated by light of equal intensity from the same source.

The Effect of using Saline Solutions in the place of Water.—We have

seen that chlorine loses its activity in the presence of ordinary water. It was found that the property in virtue of which water is able to withdraw to a limited extent the activity from chlorine was characteristic of aqueous solutions in general. Solutions of the chlorides of barium and calcium and of several acids such as hydrochloric and sulphuric were examined. In the first place, barium chloride was compared with tap water. To do this both actinometers were filled with electrolytic gas. Then they were exposed to light in order to make the gas contained in them active. After this had been accomplished, the light was turned out. Five c.c. of a strong solution of barium chloride were added to one actinometer and 5 c.c. of tap water to the other. The actinometers were shaken, allowed to stand in the dark for about half an hour, and then re-exposed to light in order to ascertain the relative lengths of the induction periods. The inert period of the gas which was standing over barium chloride was 200 minutes, whereas that of the gas over water was only forty minutes. Aqueous solutions of calcium chloride and of acids behaved as a rule in the same way as a solution of barium chloride, that is, an induction period of exceptional length attended their use. For several hours during the first stage of these long induction periods the formation of hydrogen chloride could not be detected, a fact which is in itself sufficient reason for the theory of an intermediate compound being discarded. It was observed also that solutions of different specimens of calcium chloride would absorb very different amounts of activity, but to what circumstance the observed variation was due was not at the time apparent.

Methods by which the Activity of Chlorine, Electrolytic Gas, and Solutions of Chlorine can be increased.—All the contents of an actinometer can be rendered active by maintaining the insolation vessel at a temperature approaching the boiling point of water for a sufficient length of time. Electrolytic gas can be made active therefore by raising the temperature as well as by the influence of light. Having shown this, the next step was to prove that chlorine gas becomes active under the same conditions as those required to bring about the same change in a mixture of chlorine and hydrogen. No difficulty was experienced in demonstrating satisfactorily by a suitable experiment that such was the case.

We next turned our attention to solutions of chlorine. The circumstances in which a chlorine solution will retain its inactivity or pass into the active condition are a little complex. Inactive solutions containing a large proportion of chlorine can be kept in the dark for a considerable period of time without alteration. Unlike the moist gas, a comparatively strong chlorine solution is only with difficulty rendered active by exposure to light. Such a solution, however, rapidly gains activity at the boiling point of water. It was found that when the

chlorine was withdrawn from an inactive aqueous solution by exhaustion, the liquid lost a considerable proportion of the inactivity by which it was originally characterised.

It is a curious fact that the behaviour of dilute solutions of chlorine is quite different from that of more concentrated solutions. The weak solutions gain considerably in activity on simply being kept in the dark at the ordinary temperature. The reason for this surprising difference in weak and strong solutions of chlorine is still a matter of conjecture.

The Preparation of Crystals of Active Barium Chloride.—We have already stated that different specimens of calcium chloride were found to be possessed of varying degrees of inactivity, a fact which suggested the possibility of preparing crystallised salts in an active condition. A successful attempt was made to prepare active crystals of barium chloride, the method of procedure being as follows: a strong solution of barium chloride was saturated with chlorine, heated at 100° , and the water then removed by distillation in a vacuum. The crystals which separated were active, that is, they had lost the property possessed by the original barium chloride of imparting inactivity to a dilute aqueous solution of chlorine which had previously been made active. The crystals became inactive when they were left for some time between folds of blotting paper. The last observation appeared to support the view that some vapour or gas contained in the atmosphere had been absorbed by the crystals, which thereby had been rendered inactive.

The Preparation of Active Solutions containing no Free Chlorine.—An exceedingly inactive solution of calcium chloride was saturated with chlorine, heated, and as much chlorine as possible withdrawn by exhaustion. The small amount of chlorine which remained after this treatment was then removed either by adding a little potassium iodide, and afterwards reducing the liberated iodine with a drop of sodium thiosulphate solution, or by the addition of a drop or two of sulphur dioxide solution. The solution obtained when either of these methods of removing the chlorine was employed was only slightly inactive.

The Preparation of Active Solutions without the Aid of Chlorine.—It was shown that water and aqueous solutions in general became active when they were heated with carefully purified bromine, and that after the solutions had been made active the whole of the bromine could be removed with very little loss of activity.

The Length of the Induction Period is not increased by the Presence of Oxygen in the Electrolytic Gas.—It is well known that the presence of a trace of oxygen decreases the sensitiveness* of electrolytic gas. It

* By sensitiveness is understood that quality of a sample of electrolytic gas, the degree of which is the rate of interaction of the essential components under a

was thought that the same impurity might increase the amount of induction necessary to insolate the mixture, but several comparative experiments proved that this was not the case. Electrolytic gas in fact becomes active just as rapidly when it is mixed with oxygen as when it is pure. The processes which take place during the induction period are, therefore, different in kind from those which immediately result in the formation of hydrogen chloride.

The Activity of Freshly-prepared Electrolytic Gas.—The activity of a mixture of chlorine and hydrogen prepared by the electrolysis of strong hydrochloric acid increases very considerably when the cell employed in its preparation has been in use for some time. The activity of the electrolytic gas does not fall with its sensitiveness when the acid in the cell has become weak from constant use.

It will be seen that all the preliminary experiments support the view that, as a rule, chlorine gas and many other substances, including water, contain something which will prevent chlorine and hydrogen interacting, and that the inhibitor, whether it be a quality of matter or a material substance, can be destroyed by chlorine either in the presence of light or at an elevated temperature, or by dilute chlorine solution even in the dark at the ordinary temperature. If it is a substance it is volatile, since it can be partially removed with a vacuum pump from a chlorine solution containing it.

The objection to the view that the inhibitor is a material substance is the circumstance that it appears to be possible for it to be produced spontaneously in an isolated system. The fact upon which this objection is based is, as we have already pointed out, inconsistent with the fundamental law of photochemistry, namely, that the chemical effect for a given mixture is proportional to the intensity of the illumination. So that the experiments from which the supposed fact has been deduced may possibly have been affected by some unknown source of error. However, we decided to try the effect of some of the possible impurities of water and of the crystallised salts used in the above experiments. The fact that active crystals of barium chloride became inactive when they were left between folds of blotting paper indicated that the effective inhibitive impurity (it being assumed that it is material) is contained in the atmosphere of the laboratory. The substance which appeared to satisfy best the conditions imposed by the preliminary experiments was ammonia. We therefore proceeded to investigate the influence of small quantities of this compound.

The Power possessed by Ammonia of causing an Induction Period with a Mixture of Hydrogen and Chlorine.—A solution of chlorine in aqueous calcium chloride was prepared and heated at 100° given intensity of illumination after thorough insolation. On the other hand, activity is used to designate the degree of insolation.

for several hours in order to make it active. To this solution, on cooling, a trace of ammonia was added. The solution was then divided into two portions. From one portion as much chlorine as possible was removed by exhaustion, and the other was left. Five c.c. of both portions were then respectively introduced into two actinometers. Actinometer *A* contained the solution from which the chlorine had not been pumped out, and actinometer *B* the solution from which the chlorine had been removed. The induction period with actinometer *B* was eight minutes only, and that with actinometer *A* nine hours. This experiment not only established the fact that ammonia can be the cause of a long induction period, but that the inhibitive compound produced by the interaction of chlorine and ammonia in solution at the ordinary temperature is volatile, since it can be readily removed from solution by exhaustion. The same property is, as we have already seen, characteristic of the so-called inactive solutions already examined, and no doubt these solutions mainly owed their inactivity to traces of ammonia or to some compound contained in the crystalline salts from which they were prepared and from which ammonia could easily be derived. A further experiment established the fact that a chlorine solution, which had been rendered inactive by a trace of ammonia, rapidly became active on raising the temperature to 100° , and therefore in two important particulars an exact correspondence exists between chlorine solutions to which traces of ammonia have been added and those obtained by dissolving chlorine in solutions of the chlorides of calcium and barium.

Having discovered this fact, we decided to examine several points directly arising from it; in the first place, if the induction period were in some way due to the presence in the gas of some substance which is gradually destroyed by chlorine in light, then as soon as this substance is removed there should be no return to the old state. This conclusion, however, does not accord with the experience of previous observers, or, as far as we had examined the point, with our own. By prolonged exposure of the mixed gases to light we had failed to reach a stage at which there was absolutely no return to the original condition. It is true that the rate of return after several insolutions became exceedingly slow. Was it possible that the gas could have been continuously contaminated by some impurity derived from the glass to an extent sufficient to account for the exceedingly small delay which we had been unable to eliminate entirely? It seemed to be worth our while to put this conjecture to the test of direct experiment.

For this purpose the simple actinometer shown in Fig. 2 was employed. The insolation vessel, *A*, was of quartz. The glass index

tube, *C*, carried at its end a cup, *B*, into which the neck of the quartz vessel was ground. The joint at *B* was rendered quite air-tight by pouring melted paraffin wax into the cup. As far as the rest of the apparatus is concerned the figure explains itself. The capacity of the insolation vessel, *A*, was about 70 c.c., and before filling with electrolytic gas 5 c.c. of a solution of calcium chloride were introduced. The filling with gas was effected in the following way. The liquid was emptied out of *E* and electrolytic gas was passed in a slow stream through the tube by way of the taps *F* and *G*, *A* being in the meantime heated in a bath of boiling calcium chloride solution. When it was thought that most of the air had been driven out of *A*, the tap *D* was closed and the insolation vessel cooled. Electrolytic gas was next allowed to enter the insolation vessel by cautiously opening the tap *D*.

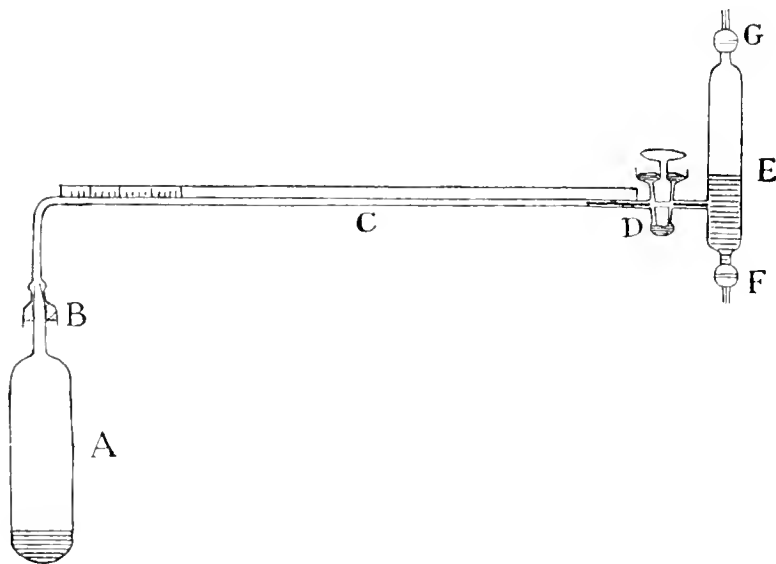


FIG. 2.

By repeating the above operations several times the apparatus was filled with electrolytic gas free from air. The tap *D* was then closed, *E* filled with chlorine water, and the apparatus was ready for use. In the last experiments relating to the present issue several probable sources of error were manifestly present. In the first place, the insolation vessel was provided with glass taps, and although the pressure of the contained gas was greater than atmospheric, some impurity may have entered through a leaking tap. In the next place, some difficulty was experienced in insulating the contents of the apparatus without at the same time admitting small quantities of fresh electrolytic gas in order to drive back the index. In the present instance, the latter imperfection was obviated by the simple expedient of connecting *G* by means of a long glass capillary tube with a large air-tight bottle immersed in the same bath as the insolation vessel.

The index could be brought thereby to any desired position by the pressure of the air within the bottle being adjusted. On first exposing the insolation vessel to light, a small induction period of a few seconds resulted, but after the contents of the actinometer had been rendered completely active by the agency of light no period of induction could be again distinguished. Even after the apparatus had been allowed to stand for more than a week in darkness, exposure of the mixed gases to light brought about immediate formation of hydrogen chloride. Instant combination manifested itself by a sudden expansion of the gases (the Draper effect), rapidly followed by a steady movement of the index towards the insolation vessel. There is therefore no decay of the activity of the mixture if the impurities which inhibit the chemical change are completely removed and care is taken to prevent the contamination of the gases with fresh impurity. The knowledge of this fact is of supreme importance, for we are no longer able to look upon the formation of intermediate compounds as being in any sense accountable for the phenomenon of photochemical induction.*

There was another point awaiting a more careful examination than we had hitherto been able to give to it. Attempts had been made to remove the chlorine completely from an active solution without at the same time rendering the solution inactive. In this we had only been partially successful, owing no doubt to the reagents added to remove the last traces of chlorine containing small amounts of some impurity capable of preventing the combination of chlorine and hydrogen in light. In order to avoid this source of error, an experiment was performed in the following way. A 20 per cent. solution of calcium chloride was saturated with chlorine, heated, and the chlorine removed as far as possible by exhaustion. The rest of the chlorine was extracted from the solution by digesting it with silver gauze in a Soxhlet's apparatus for two days. On adding 5 c.c. of the resulting liquid to an actinometer which contained previously insolated electrolytic gas, and then exposing the insolation vessel to light, we were unable to perceive any signs of an induction period. The liquid from the Soxhlet's apparatus was shown to be free from chlorine by testing it with potassium iodide and starch.

The Relation between the Quantity of Ammonia used and the Magnitude of the Effect produced by it.—In the experiments on this point a Harcourt standard pentane lamp of ten candle units placed at a distance of 50 cm. from the insolation vessel served as the means by which constant illumination was secured. To the actinometer, after it had been filled with active electrolytic gas, 5 c.c. of a very dilute solution of ammonia were added. The liquid having been introduced,

* Incidentally some of the theories formulated with the purpose of explaining the action of water are deprived of much of their force.

the actinometers were shaken and allowed to stand in the dark for some time before being exposed to light.

In order to obtain dilute solutions of ammonia of known strength, a sample of water free from ammonia and from organic compounds capable of yielding ammonia had first to be prepared

The Removal of Ammonia and Organic Impurities from Water.—The apparatus, Fig. 3, was used. The flask, *A*, was filled with a solution of 8 grams of potassium permanganate in 500 c.c. of dilute sulphuric acid. The mixture was gently heated for twelve hours over the water-bath. The flask was then connected, as shown in the diagram, with the reservoir, *B*, and the whole apparatus exhausted with

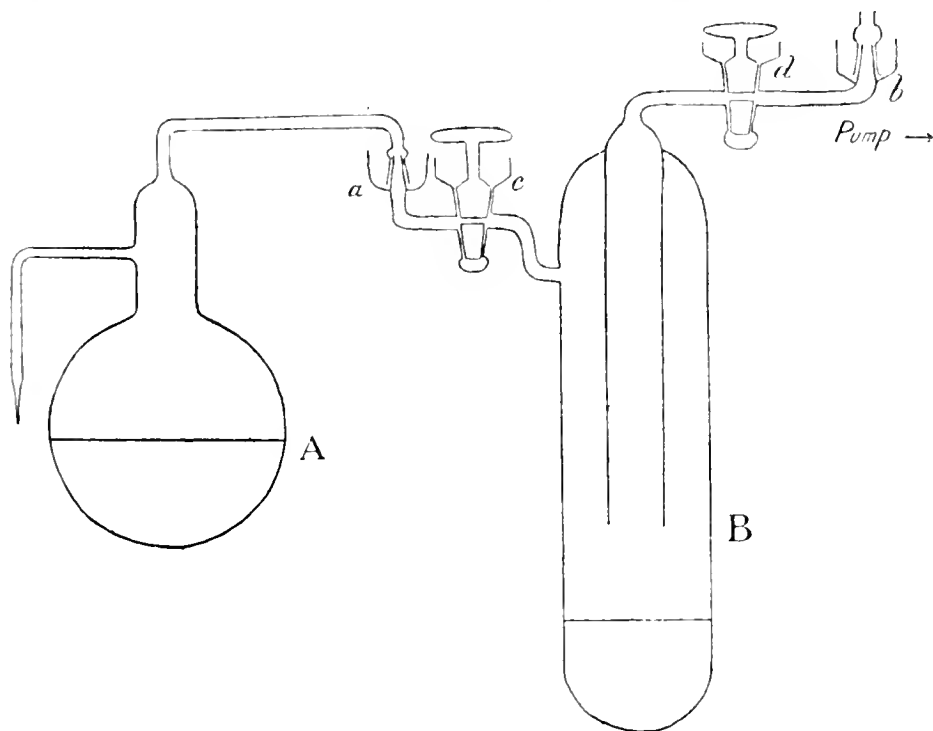


FIG. 3.

a Sprengel mercury pump. The receiver was next surrounded with a freezing mixture and water distilled from *A* to *B* without the application of heat. When sufficient had distilled over, the taps *C* and *d* were closed, the receiver disconnected at the ground glass connections, and the water which it contained immediately tested in a previously filled actinometer. The actual readings of the index scale taken at intervals of two minutes were as under :

Time.	Reading.	Movement.	Time.	Reading.	Movement.
0	18.45	—	10	39.50	7.50
2	18.70	0.25	12	47.20	7.70
4	20.00	1.30	14	55.20	8.00
6	25.20	5.20	16	63.20	8.00
8	32.00	6.80			

In the meantime the water in the receiver was allowed to stand in contact with the air which had been admitted when the portion for testing had been removed. With the water thus contaminated, a second experiment was performed several hours afterwards. The result is recorded below :

Time.	Reading.	Movement.	Time.	Reading.	Movement.
0	0.35	—	12	8.50	4.75
2	0.00	-0.35	14	13.50	5.00
4	0.05	0.05	16	18.80	5.30
6	0.25	0.20	18	21.10	5.30
8	0.75	0.50	20	28.80	4.70
10	3.75	3.00			

The effect of contamination with atmospheric impurities is manifest.* With a sample of the so-called ammonia-free water obtained by the method commonly adopted in water analysis, the following numbers were obtained:

Time.	Reading.	Movement.	Time.	Reading.	Movement.
0	16.1	—	16	16.0	0.4
2	15.8	-0.3	18	17.0	1.0
4	15.8	0.0	20	18.7	1.7
6	15.6	-0.2	22	25.0	5.3
8	15.6	0.0	24	31.0	6.0
10	15.4	-0.2	26	39.8	8.8
12	15.4	0.0	28	49.9	10.1
14	15.6	0.2			

With the distilled water used in the laboratories for analysis, the induction period varied from forty to fifty minutes.

Solutions containing known amounts of ammonium chloride in the purest obtainable water were next made, and the resulting effect of the addition of 5 c.c. of these solutions to the actinometer was automatically recorded in the manner already described. When 5 c.c. of solution contained 0.0000036 gram of ammonia, the induction period was one hour and forty-nine minutes. When the 5 c.c. of solution contained 0.0000083 gram of ammonia, the induction period was three hours and thirty-seven minutes. When the 5 c.c. of solution contained 0.00004 gram of ammonia, the induction period was sixteen hours and seven minutes.

For small quantities of ammonia, the length of the induction period appears to be roughly proportional to its amount.

The discovery of the fact that the presence of ammonia or of some unstable substance directly derived from the interaction of ammonia and chlorine is at any rate one of the causes of the phenomenon known as the period of photochemical induction led us to try the effect of other impurities which are capable of reacting with and of being gradually

* In the preparation of the pure water, care was, of course, taken to use only such materials as were free from chloride.

removed by chlorine. The examination of this point occupied several months, and proved to be more difficult than we had anticipated. The principal obstacle was in obtaining compounds free from ammonia or from substances capable of yielding ammonia on decomposition. It was at first thought that one or two of the substances included in the following list exerted an influence similar to, although not so great as, that of ammonia on the combination of hydrogen and chloride, but this was ultimately traced to the presence of impurities in the compounds in question. The addition of the following substances to a mixture of chlorine and hydrogen does not prevent action between those gases from taking place in the light : *

- | | |
|----------------------------|------------------------------|
| (1) Alcohol. | (7) Nitric acid. |
| (2) Ether. | (8) Stannous chloride. |
| (3) Benzene. | (9) Hydrogen peroxide. |
| (4) Sulphur dioxide. | (10) Potassium permanganate. |
| (5) Sulphuretted hydrogen. | (11) Aqua regia. |
| (6) Nitrous acid. | |

We must now give a short space to the consideration of an apparent discrepancy between the results of some of our earlier experiments and the recent observations concerning the specific effect of traces of ammonia. It had been repeatedly noticed that, even after the contents of an actinometer had been so well insulated that after the insulation vessel had been shaken and then immediately exposed to light no indication of an induction period could be obtained, a distinct decay of activity took place in the dark after the lapse of a few days. This fact could not be explained by the assumption that ammonia is the only substance which will completely prevent the interaction of hydrogen and chlorine. For the combination of the chlorine and hydrogen could not have proceeded at a steady pace in the first instance until the whole of the ammonia had been destroyed, and as soon as this state of affairs had been reached there was no conceivable mode by which the system could have returned to its old condition. The effect to which we refer could not be observed when a solution of ammonium chloride in pure water was used to inhibit the reaction between chlorine and hydrogen. If, however, water from which the organic impurities had not been carefully removed was employed in a similar experiment, the so-called decay of activity occurred after the actinometer had stood for some hours in the dark ; and, accordingly, impure water as a general rule contains besides ammonia other impurities capable of yielding after a time, when submitted to the action of chlorine, com-

* Aniline and dimethylaniline appear to act inhibitive. Up to the present, however, their specific effect has not been made the subject of a comprehensive inquiry.

pounds which will prevent that element from combining with hydrogen in the light. Since several organic compounds free from nitrogen had been tested, and found not to exert an influence similar to that of ammonia, it was thought that the impurities contained in water, and to the presence of which the effect in question is due, must be nitrogenous substances capable of yielding ammonia on oxidation. This conjecture was shown to be correct by an experiment with egg albumen: 0.01 gram of egg albumen was dissolved in 100 c.c. of water, and 5 c.c. of this solution were tested in an actinometer in the usual way. On exposure to light there was an induction period of one hour. The next day, after standing in the dark for sixteen hours, the induction period was one hour and fifty-four minutes, or almost twice as long as that observed when the insolation vessel was first exposed to light. A third exposure on the day following resulted in a period of inertness of one hour and forty-five minutes. It has been already stated that no such effect can be observed when for the solution of albumen one of ammonia in pure water is substituted; in such circumstances, the second induction period is always considerably shorter than the first. This gradual decomposition of the nitrogenous organic substances in an aqueous solution of chlorine was undoubtedly the cause of our inability in the first instance to demonstrate the non-existence of the so-called decay of activity, and is mainly responsible for the erroneous views concerning the period of chemical induction which have prevailed for half a century.

Before passing on to the consideration of another aspect of the problem of the combination of chlorine and hydrogen, one other obscurity must be removed. In the first experiment demonstrating that a pure mixture of moist chlorine and hydrogen responds immediately to the action of light, an actinometer with an insolation vessel constructed of quartz was used. At the time it was thought that the result was due to the circumstance that quartz had been substituted for glass. Knowing as we did the inhibitive effect of minute traces of ammonia, we thought that it was not impossible that some impurity capable of preventing for a time the combination of chlorine and hydrogen might be produced by the action of chlorine on glass. It has, however, been shown that the experiment can be equally well performed in an apparatus constructed entirely in glass, and that the successful result with the quartz actinometer was really due to the fact that in filling it with electrolytic gas the liquid contained within it had to be heated for some time in the presence of chlorine, an operation which would clearly result in the destruction of those nitrogenous organic compounds most likely to yield substituted ammonias on standing with chlorine. We shall now discuss another important class of facts directly connected with the subject.

Expansion Experiments.

The experiments of C. T. R. Wilson on cloud formation suggested to Bevan the desirability of investigating the subject in the light of the known facts concerning the formation of clouds in suddenly expanded gases saturated with water vapour. We may say that our experience in this department of the subject coincides closely with that of Bevan, but we hope to be able to show that the facts will bear an interpretation consistent with the views developed in this paper. Briefly, what Bevan found was this. Firstly, that when strongly illuminated chlorine is suddenly expanded a fine rain appears at an expansion of 1.30,* and a cloud at an expansion of 1.46, whereas with darkened chlorine the cloud does not appear until an expansion of 1.50 approximately is made. Secondly, that when darkened electrolytic gas is expanded, only a few drops can be observed with an expansion of less than 1.42, whereas with the illuminated gas, drops begin to be formed at an expansion of 1.22 and a thick cloud is formed at an expansion of 1.36. Thirdly, that if, after hydrochloric acid has begun to be formed, an expansion is made, the formation of hydrochloric acid stops if the expansion is large enough to produce a cloud. These are the principal facts established by Bevan, and from them in conjunction with others of secondary importance he draws the following conclusions :

(1) When chlorine is strongly illuminated, condensation nuclei are produced, these nuclei being the cause of the cloud appearing at a less expansion in the illuminated than in the non-illuminated gas. The nuclei are addition compounds of the type $\text{Cl}_2, \text{H}_2\text{O}$.

(2) Condensation nuclei are also the cause of the difference which was observed with illuminated and non-illuminated electrolytic gas, but in this case the nuclei are addition compounds of chlorine water and hydrogen, of the type $\text{Cl}_2, \text{H}_2\text{O}, \text{H}_2$, which are formed by the combination of hydrogen molecules with the complexes $\text{Cl}_2, \text{H}_2\text{O}$. The hydrochloric acid is formed by the breaking down of the addition compound $\text{Cl}_2, \text{H}_2\text{O}, \text{H}_2$ into water and hydrochloric acid.

(3) The removal of the condensation nuclei by the formation of a cloud will clearly at the same time remove the molecules from which hydrogen chloride can alone be formed, and for this reason the gas becomes inactive after the cloud has subsided.

There are indications that the facts will not bear the interpretation given to them by Bevan. For, in the first place, evidence of the formation of condensation nuclei in moist chlorine could only be obtained

* The number 1.30 is the ratio of the pressure before expansion to that after expansion.

when a strong light was used to illuminate the gas, whereas nuclei were found in electrolytic gas when the illumination was feeble, a fact not in good accord with the theory, which postulates that the nuclei of electrolytic gas are directly formed from those of chlorine by the addition of molecules of hydrogen. A simple deduction from the theory would be that nuclei should be formed in chlorine at least as readily as in electrolytic gas. The circumstance that a much stronger illumination is required to produce nuclei in chlorine gas than in a mixture of hydrogen and chlorine points to the conclusion that the difference observed in the light and dark is due in both cases to the formation of hydrochloric acid in the light. We shall return to the consideration of this point after describing our own experiments.

The first question requiring further examination was this. Does the formation of a cloud by expansion in electrolytic gas, which has by exposure to light acquired the property of instantly combining in light, deprive the gas of the power which it has gained? At the time that Bevan attempted to answer this question, the available information which could be brought to bear on its solution was not sufficiently detailed to prevent mistakes being made. Bevan, it is true, had made the important discovery that by washing insulated electrolytic gas with water it re-acquired the properties which it possessed before insulation, but it was not known that when a vessel containing both water and electrolytic gas is exposed to light the gas and the water immediately in contact with it can become active without the rest of the water being much affected, so that a disturbance such as that produced by making an expansion could bring the inactive liquid into contact with the gas with an obvious result. However this might be, Bevan's experiment had to be repeated, avoiding the source of error here indicated.

In the experiments relating to this point, Wilson's expansion apparatus was not used owing to the obvious difficulty of insulating the chlorine. The apparatus employed is depicted in Fig. 4. The insulation vessel, *A*, contained a few c.c. of water almost free from ammonia.

The air in the apparatus was first displaced by chlorine, which was heated for some time with the liquid contained in it in order to destroy the impurities. The chlorine was next displaced by a mixture of hydrogen and chlorine, and exposed to light until all the objectionable impurities contained in the gas had been destroyed. It could easily be decided when this had been accomplished by allowing the actinometer to stand for some time in the dark and then re-exposing to light, when the gases should instantly expand owing to the immediate formation of hydrochloric acid. An experiment was performed in the

following way. An amount of liquid sufficient to serve as an index was transferred from *A* to *B*. The taps *a* and *b* were closed, and *B* partially exhausted. When it was thought that the exhaustion was sufficient, *c* was closed and *a* suddenly opened. A cloud was produced in *A* by the sudden expansion, which subsided more or less rapidly according to the size of the drops contained in it. When an expansion of more than a given amount is made, a fog consisting of numberless minute drops is produced. These drops evaporate long before they can fall to the bottom of the vessel. Immediately after making the expansion, the tap *a* was closed and *b* opened. On exposing *A* to light, instant combination, as indicated by an immediate expansion of the gas, occurred. By varying the expansion and also the length of time from

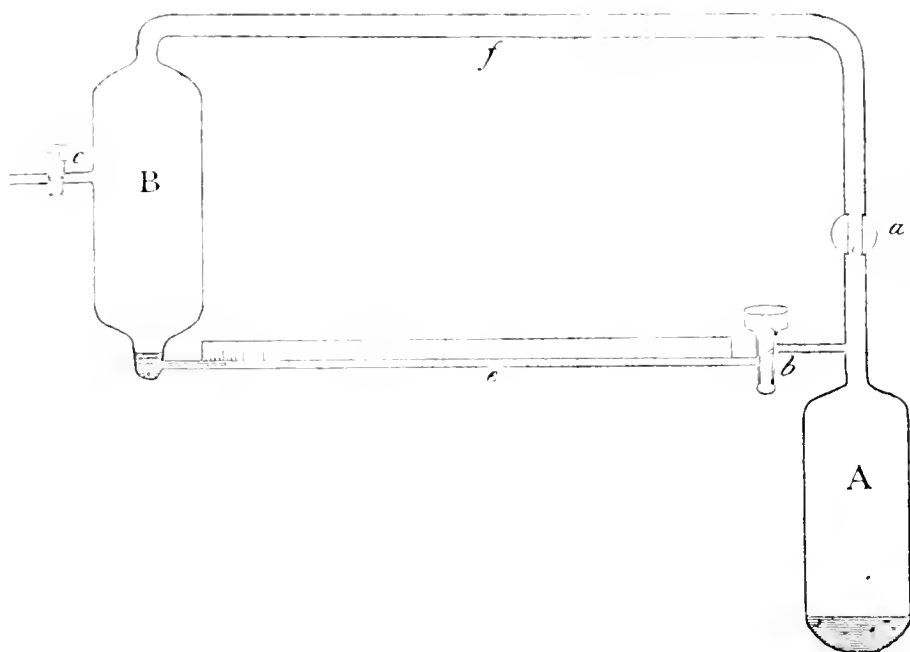


FIG. 4.

the expansion to the exposure to light we were unable to observe any departure from the above result. So that when due consideration is given to the necessity of completely insulating both the liquid and the gas, no evidence of molecules of an intermediate compound capable of acting as condensation nuclei could be obtained.

The Formation of Clouds in Illuminated and Darkened Chlorine.—The apparatus, as will be seen from the diagram, Fig. 5, was similar in principle to one described by C. T. R. Wilson (*Phil. Trans.*, 1897, 189, 276). Several modifications had, however, to be introduced owing to the special circumstances of the experiments and the limitations imposed by the use of chlorine. The expansion vessel, *A*, was provided with a loosely-fitting piston, *B*. It is essential that the convex base of the piston should be carefully ground so as to fit exactly the lower

portion of the expansion vessel, otherwise the liquid used to lubricate the piston and prevent the escape of gas is liable to be drawn out on making an expansion. The part of the apparatus above *A* is designed for the double purpose of containing the liquid for lubricating the piston and a supply of the gas to be experimented upon. The expansion is made with the portion of the apparatus shown on the left of the figure. Direct communication between the expansion chamber, *A*, and the evacuated bottle, *K*, can be established by removing the rubber

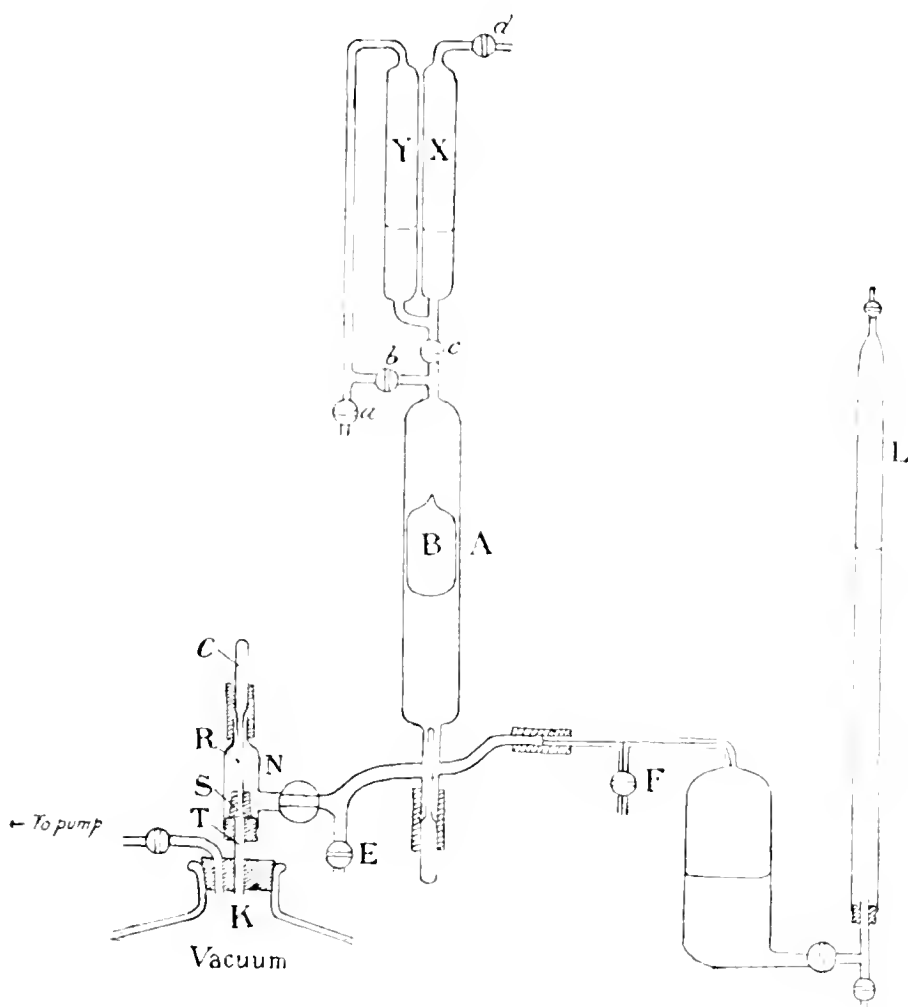


FIG. 5.

stopper, *S*, from the mouth of the tube, *T*, which it closes. The sudden reduction of pressure thus effected causes the piston rapidly to descend. The glass rod, *R*, with which the stopper, *S*, is raised and lowered passes through the constricted upper portion of the tube, *M*, the opening being rendered air-tight by means of the rubber tube, *C*. The part of the apparatus shown on the right of the figure is a pressure gauge, the pressure being deduced from the volume occupied by a fixed quantity of air enclosed in the burette, *L*. A mercury gauge can be used, but

the inconveniences attending its use with chlorine are considerable. An expansion of any desired amount can be made in the following way. The piston is raised by pumping air into the apparatus through the tap *E*. For this purpose an ordinary bicycle pump with an india-rubber valve is used. The tap *E* is next closed and the pressure recorded. The expansion is then made in the manner already described. In order to measure the pressure in the expansion chamber after an expansion has been made, air is cautiously admitted through the capillary tap *F*, the piston being in the meanwhile carefully observed. As soon as the piston rises the pressure is again noted. If P_1 is the pressure in the expansion chamber before, and P_2 that after expansion, then P_1/P_2 is the desired ratio. The general characteristics of a cloud produced by an expansion are readily distinguishable when viewed either by yellow or by white light.

In order to test if our apparatus would give results similar to those obtained by Wilson, a few expansions were made with moist air in the expansion chamber. The few recorded observations are in good agreement with those taken from Wilson's paper, as a comparison of the following statements will show.

P_1/P_2 .	Character of cloud.
1.366	Rain falling in ten seconds.
1.383	Fog, drops taking about one minute to fall.
1.395	Fog, disappeared by evaporation.
1.414	Beautiful greenish-blue fog.

Wilson obtained the following results :

P_1/P_2 .	Character of cloud.
1.378	Colours scarcely visible, drops settled in a few seconds.
1.385	Rings brilliant, took several minutes to settle.
1.419	Bluish-green fog.

The apparatus was filled with chlorine in the following way. A suitable amount of liquid was first introduced into *X* and *Y*. Chlorine gas was then passed in at the tap *a* and out at the tap *d*. In the meantime *b* was left open and *c* closed. To ensure the complete displacement of the air in the expansion chamber, the piston was moved slowly up and down whilst the chlorine was being led through the apparatus. The time occupied in filling the apparatus is considerably shortened if the liquid which it contains is saturated with chlorine before introduction. Whilst the expansions are being made, the tap *c* must be occasionally opened and a small amount of water allowed to run down on to the piston for the purpose of lubrication. If the grinding at the bottom of the expansion chamber is thorough it is only necessary to introduce fresh liquid after every four or five expansions.

With chlorine alone, six series of measurements were made: three when the lubricating liquid was ammonia free, and three when it contained ammonia. In both cases the three series of observations were in bright white light, in white light of moderate intensity, and in yellow light. The intense white light was obtained by concentrating the rays from a 25 c.p. electric lamp on the expansion chamber by means of a large flask of cold water. The moderate illumination was produced by the same lamp placed at a distance of 50 cm. from the expansion chamber and with the interposition of a water lens. The yellow light was obtained by filtering white light through a solution of potassium bichromate, the light being subsequently passed through a vertical slit 2 mm. broad and 2 cm. long. By employing a narrow beam of light, the character of the cloud is more easily discerned, and at the same time the total amount of light falling on the chlorine is reduced. The results are tabulated below:

I. *A Solution of Chlorine in Ammonia-free Water was used to Lubricate the Piston.*

Character of cloud.	Expansion = P_1/P_2 .		
	Strong white light.	Moderate white light.	Yellow light.
Fine rain.....	1.30—1.33	1.38—1.42	1.42—1.44
Rain	1.33—1.38	1.42—1.46	1.44—1.46
Rain cloud	1.38—1.42	1.46—1.48	1.46—1.48
Thick „	1.42—1.45	1.48—1.50	1.48—1.50
Fog	1.46	1.51	1.51

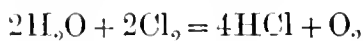
II. *A Solution of Chlorine in Water containing Ammonia was used to Lubricate the Piston.*

Character of cloud.	Expansion = P_1/P_2 .		
	Strong white light.	Moderate white light.	Yellow light.
Fine rain.....	1.30—1.35	1.40—1.43	1.40—1.45
Rain.....	1.35—1.38	1.43—1.47	1.45—1.46
Rain cloud	1.38—1.41	1.47—1.49	1.46—1.48
Thick „	1.41—1.43	1.49—1.50	1.48—1.50
Fog	1.45	1.51	1.51

The results obtained with a moderate light when compared with those obtained with a yellow light are instructive. They are practically identical and furnish no evidence of the formation of condensation nuclei, although the intensity of the white light was certainly sufficiently great to cause rapid combination of hydrogen and chlorine. If the first step in the formation of hydrochloric acid from a moist mixture of chlorine and hydrogen were the production of molecules of the type $\text{Cl}_2\text{H}_2\text{O}$ capable of acting as condensation nuclei, it ought clearly

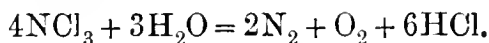
to be possible to obtain some evidence of their formation when moist chlorine is illuminated with white light of the intensity mentioned.

The effect of the light is only apparent when its intensity reaches a value at which it is conceivable that the reaction represented by the equation



proceeds at an appreciable rate, that is, when hydrochloric acid is formed rapidly enough to increase materially the extent of supersaturation. The formation of hydrochloric acid within a moist gas would clearly aid the condensation of moisture, and if an expansion were made when a tendency to condensation already existed it is obvious that a less expansion would be required to reach that degree of supersaturation at which a cloud is formed than if that tendency did not exist. There is in fact so far as we can see no sufficient reason for rejecting this simple explanation of the facts.

There is one other circumstance worth noting, namely, that the introduction of ammonia into the system does not retard but, if anything, facilitates the formation of a cloud. Such a fact might be taken to indicate that the presence of ammonia or of the substituted ammonias does not prevent the reaction between water and chlorine from taking place. It must not, however, be forgotten that hydrochloric acid can arise from the interaction of ammonia or of the partially substituted ammonias and chlorine. There is a further possibility of hydrochloric acid being produced by the interaction of nitrogen trichloride and water in accordance with the equation



The expansion experiments with a mixture of chlorine and hydrogen lend additional support to the view here expressed, that the difference observed in the light and in the dark is really due to the greater degree of supersaturation resulting from the formation of hydrochloric acid in the former case. Two series of measurements were made. In the first the liquid used to lubricate the piston was obtained from water containing ammonia, and in the second from ammonia-free water. The light was a 25 c.p. incandescent lamp placed at a distance of 50 cm. from the expansion chamber. In other respects the two series of observations were made under precisely similar conditions.

Below are the tabulated results:

Character of cloud.	Expansion = P_1/P_2 .	
	With ammonia.	Without ammonia.
Fine rain	1.38—1.42	1.30—1.38
Rain	1.42—1.43	1.33—1.35
Rain cloud	1.44	1.35
Thick „	1.46	1.36
Fog	1.47	1.37

When the expansions were made in the dark, results practically identical with those in the first column of the above table were obtained with the ammonia-free gas.

It will be observed that a cloud is formed at a lower expansion both in chlorine and electrolytic gas only in such circumstances as are known to favour the formation of hydrogen chloride, and it is therefore not unreasonable to suppose that the increased tendency to form a cloud is directly due to a state of supersaturation set up by the continuous production of hydrogen chloride in the presence of water vapour.

It is probable that charged ions, or at any rate molecules differing from the ordinary molecules of which the gases are mainly composed, may yet be discovered either in chlorine or in electrolytic gas when subjected to the influence of light, but at present we believe that neither Bevan's experiments nor our own furnish sufficient evidence of the formation in illuminated chlorine of condensation nuclei differing essentially in character from those present under all conditions in the gas.

Experiment relating to the Extinction Coefficient.

It has at various times, and by more than one authority, been asserted that a definite proportion of the rays absorbed during chemical change are expended in bringing about the change. Bunsen and Roscoe interpret some of their experiments with the aid of the assumption that the absorbed rays can be divided into two distinct parts, those which are absorbed by the substances in the mixture in virtue of their optical properties and those which effect the chemical changes. If this view were correct, then a mixture of air and chlorine in equal proportions would absorb less light than a mixture of hydrogen and chlorine. Bunsen and Roscoe claim to have shown experimentally that such is the case, but their work is open to one serious objection. For want of precise information on the point, they were compelled to assume that a formula which is only strictly applicable for monochromatic light could for all practical purposes be used in interpreting the results of experiments performed with composite light.

This weakness was recognised at the time by Bunsen and Roscoe, and the practical validity of the approximation made by them has since been called in question by Pringsheim and others. Up to the present time, however, no attempt has been made to settle the disputed point by a further appeal to experiment.

The question has been re-examined by us, using a method free from the objection indicated above. The results point to the conclusion that if there is any difference in the relative transparency of a

mixture in equal proportions of air and chlorine and of electrolytic gas, it is of an order of magnitude not detectable by the means at present at our disposal. A short description of our mode of working must be here included.

The insulation vessel, *I*, was enclosed in a bath constructed of sheets of plain glass. The tank was surrounded with felt, and was provided with a felt cover. The light was admitted through a window, *a b*. The index reservoir of the actinometer communicated with a large bottle, *X*, immersed in the bath. The water in the bath was stirred by a current of air blown in at the bottom, and its temperature was maintained constant by means of an electric thermo-regulator controlling an incandescent electric lamp placed in the same bath. The liquid used in the thermo-regulator was olive oil, and the U-tube, *A*, containing this liquid was also filled with pieces of copper gauze in order to ensure the rapid conduction of heat from the walls to the interior.

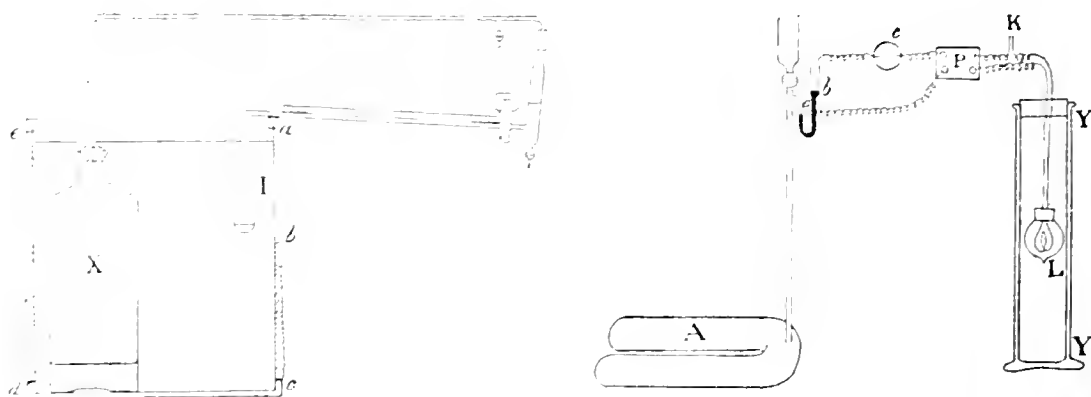


FIG. 6.

The expansion of the oil drove a narrow thread of mercury in the capillary tube, *a b*, downwards, and broke contact at *a* between a platinum wire fused into the walls of the capillary tube and the mercury. The other end of the thread of mercury was in continuous connection with a wire thrust down the tube. The wires at *a* and *b* were the terminals of a circuit, including a small storage cell, *c*, and a post-office relay, *P*. The lighting circuit, including an 8 c.p. incandescent lamp, *L*, was closed and opened by the relay according as the wire at *a* was or was not in contact with the thread of mercury. The lamp was enclosed in an opaque cylinder, *Y*, and immersed in the bath with the thermo-regulator. During the experiment the temperature never varied more than 0.02° . The need for maintaining the temperature constant will be evident when it is remembered that a slight variation in the composition of the mixture enclosed in the insulation vessel owing to a disengagement of chlorine from the solution may cause considerable variations in the sensitiveness of the instrument.

A troublesome source of error is one already indicated in the account of our preliminary experiments. We allude to the disengagement of chlorine which takes place owing to the production of hydrochloric acid, and which manifests itself by an expansion after the light is shut off. The effect of this source of error is, of course, to increase the initial readings. When water is used in the insolation vessel to absorb the hydrochloric acid, it is frequently, owing to this cause, impossible to obtain constant readings until the index liquid has moved through almost the whole length of the index tube, and is about to enter the insolation vessel. At the outset, accordingly, experiments had to be performed in order to discover an absorbent liquid less liable to this objection. A mixture of four parts of strong hydrochloric acid to one of water was found to serve the purpose. When this solution was used, the expansion on standing in the dark was not more than $1/30$ th, whereas with water it may even be greater than the total volume of hydrochloric acid formed. The error here indicated is, of course, decreased by reducing the intensity of the light.

Another point to bear in mind is the necessity of completely destroying all those substances which can give rise to an induction period. If this is not attended to the instrument is liable to become more sensitive during use.

It is best to fill the actinometer with a mixture containing an excess of one or other of the gases, as a slight variation in the composition of the mixture will then affect to a less degree the indications of the instrument.

The apparatus used to contain the gas whose extinction coefficient it was desired to measure is depicted in Fig. 7. It consisted of a hollow glass cylinder with a circular rim at both ends. Two plates, B_1 and B_2 , were ground at their edges to fit the ends of the cylinder, the joint between the cylinder and the plates being made air-tight with a layer of Faraday cement on the outside. The cylinder was provided with two taps, a and b , for filling. The taps were lubricated with vaseline, which does not interfere with the reaction between hydrogen and chlorine. Two metal cylinders, c_1 and c_2 , with circular apertures, x_1 x_2 and y_1 y_2 , enclosed the apparatus. The cylinder was interposed between the source of light and the insolation vessel with its plane faces at right angles to the incident beam, and was firmly clamped in position during an experiment. The distance between the glass plates was 60 mm. In filling the apparatus with electrolytic gas, all the obvious precautions necessary to obtain a sensitive mixture were observed, and, as a matter of fact, a very fair estimate of the character of the mixture was obtained by affixing an index to the exit tube and observing the magnitude of

the Draper effect. The Draper effect for a light of given intensity is roughly proportional to the sensitiveness of the mixture.

The first series of experiments was performed with a moist mixture of hydrogen and chlorine, but these had to be abandoned owing to the circumstance that as soon as light fell upon the mixed gases a deposit of dew was formed on the glass plates, which intercepted part of the light. Gases dried with sulphuric acid were therefore used.

Experiment I.—The source of light was an 8 c.p. incandescent lamp. The voltage at the terminals of the lamp oscillated slightly, but the

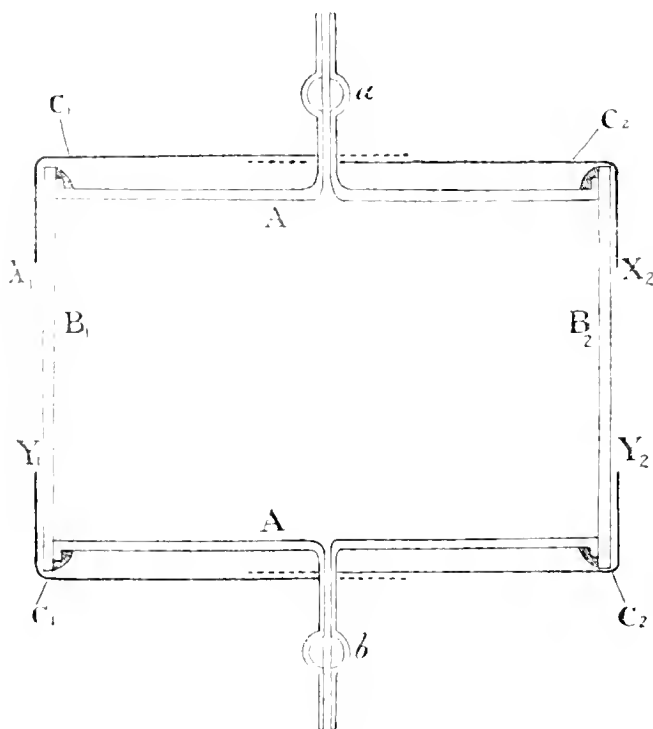


FIG. 7.

mean value was constant. The lamp was at a distance of 84 cm. from the insulation vessel and 50 cm. from the nearest plate of the extinction apparatus. The air in the extinction apparatus was first displaced by chlorine, the chlorine being in its turn displaced by electrolytic gas, which was let in at the top and out at the bottom of the apparatus. After the gas had been passing through for three hours, a series of measurements was made. At the end of a further three hours a fresh series of readings was taken, the stream of gas being in the meanwhile continued. The results are contained in the subjoined table :

<i>After 3 hours.</i>					<i>After 6 hours.</i>				
1...	7.45	cm.	in 10 minutes		1 ..	7.50	cm.	in 10 minutes	
2...	7.25	"	"	"	2...	7.60	"	"	"
3...	7.35	"	"	"	3...	7.50	"	"	"
<hr/>					<hr/>				
Mean...	7.35	"	"	"	Mean...	7.53	"	"	"

The mixed gases were now displaced by air dried with sulphuric acid. The barometer at the end stood at 770 mm. A manometer was affixed to the apparatus and the air removed with the water pump until the pressure in the apparatus was 385 mm. Dry chlorine was then admitted, the supply of gas being shut off as soon as the pressure had reached that of the atmosphere. Three-quarters of an hour was allowed for the gases to mix, and then readings were taken. These are recorded below.

1.....	7.40	cm.	in 10 minutes
2.....	7.25	"	"
3.....	7.00	"	"
4.....	7.15	"	"
<hr/>			
Mean.....	7.20	"	"

The temperature of the bath during this experiment was 19.90°.

Experiment II.—In this experiment the source of light was a Harcourt 10 c.p. pentane lamp. In other respects the conditions were similar to those in the last experiment. Summing the readings we obtain the result :

Movement of index with electrolytic gas in the extinction apparatus, 42.90 cm. in forty-five minutes.

Movement of the index with a mixture of chlorine and oxygen in the apparatus, 43.60 cm. in forty-five minutes.

The ratios of the mean readings obtained with electrolytic gas to those obtained with a mixture of chlorine and oxygen in the two experiments are :

<i>Experiment I.</i>		<i>Experiment II.</i>
1.034		0.984

The variation from equality is in both cases within the errors of experiment. It is a simple matter to calculate what the above ratio should be if the coefficients of extinction of electrolytic gas and of a mixture of equal volumes of chlorine and oxygen were what Bunsen and Roscoe found them to be.

The formula giving the intensity of the incident and emergent beam is

$$a(\log_{10} I_0 - \log_{10} I) = x,$$

where I_0 and I are the intensities of the respective beams and a is the length of gas which must be traversed by the light in order that its intensity may be reduced ten-fold, and x is the length actually traversed.

Now the value of a for electrolytic gas is given by Bunsen and Roscoe as 262 mm. and that for a mixture of equal volumes of oxygen and chlorine as 346, and therefore in the present case,

$$\begin{aligned} 262 (\log_{10} I_0 - \log_{10} I) &= 60 \\ \text{and } 346 (\log_{10} I_0 - \log_{10} I') &= 60, \end{aligned}$$

where I is the intensity of the beam emerging from the hydrogen and chlorine, and I' that from the oxygen and chlorine. Eliminating I_0 , we find

$$262 \times 346 (\log I' - \log I) = 60 \times 112 ;$$

when, making I' equal to unity, I becomes 0.879; that is, a difference which could be detected with certainty by means of the actinometer. In arriving at the above conclusion concerning the difference in the value of the extinction coefficients for mixtures composed of equal volumes of hydrogen and chlorine and of oxygen and chlorine, Bunsen and Roscoe assumed that the amount of chemical change for a given mixture of hydrogen and chlorine was proportional to the light absorbed, and that the relation subsisting between the two quantities was the same for light of all refrangibilities. The second half of the above assumption is probably not correct, and, indeed, if this is admitted it is unnecessary to suppose that either Bunsen and Roscoe's results or our own are affected by any serious experimental error, since the discrepancy in the conclusions is then easily accounted for.

Our experiments tend to show that the light absorbed by mixtures of chlorine either with hydrogen or with an inert gas such as oxygen is almost the same as it would be if the same beam of light were made to traverse the same column of chlorine from which the diluting gas had been removed. There is no indication that the light which brings about the chemical change is distinct from that absorbed by the chlorine in virtue of its optical properties. The energy which brings about the chemical change is derived from the light absorbed by the moist chlorine.

From the above measurements, it might be concluded that the extinction coefficient of a mixture of gases is an additive property, if it were not for the fact that Mellor has found that dry chlorine is considerably more transparent to those rays which bring about the interaction of hydrogen and chlorine than the moist gas, and Mellor's statement to this effect is supported by the fact that dry

chlorine refuses to give any indication of the Budde expansion. From the measurements given in Mellor's paper we have calculated the extinction coefficient of his dry chlorine, and find that it is not greatly different from the value given by Bunsen and Roscoe, who used chlorine which had not been very carefully dried. Further experimental inquiry on this important point is necessary before any definite conclusions can be drawn.

In dealing with extinction coefficients, it would probably not be out of place if we drew attention to a research performed with great care and precision by M. Wildermann (*Phil. Trans.*, 1902, 199, 337), in which, as it appears to us, the dependence of the amount of chemical change on the quantity and character of the light absorbed has not been taken sufficiently into consideration. The object of the author was, as he states, to ascertain, if possible, the laws governing the velocity of chemical reaction and chemical equilibrium when the change is caused by the introduction of light energy into the system. Mixtures of carbon monoxide and chlorine in different proportions were enclosed in a vessel of about $3\frac{1}{2}$ cm. diameter, which was provided with a manometer. The vessel was exposed to the rays of an acetylene lamp, and the progress of the reaction noted by watching the indication of the manometer. The reaction during the normal period was shown to follow with close approximation the well-known law of mass, expressed by the equation

$$dx = k(A - x)(B - x)dt,$$

where x is the amount of chemical change, A and B the initial quantities of chlorine and carbon monoxide respectively, k a constant, and t the time. Wildermann concludes that photochemical reactions are governed by the same law of mass as reactions which take place in the dark. Now the results of Draper and of Bunsen and Roscoe with hydrogen and chlorine most explicitly contradict this result. For these authorities have proved that the rate of combination of a mixture of chlorine and hydrogen in equivalent proportions is very considerably reduced when the proportion of either of the reacting gases is increased to a small extent. Whether the same peculiarity characterises the behaviour of a mixture of equivalent quantities of carbon monoxide and chlorine we cannot say, as the literature contains no information upon this point. But, in any event, Wildermann's general statement appears to be contrary to the results of direct experiment. Moreover, there are other considerations which would lead us to doubt the validity of drawing this conclusion from the results of Wildermann's experiments. We will, for the sake of simplicity, suppose that the light is monochromatic. In such circumstances the amount of action in unit

time for a parallel beam of unit section acting on a mixture of constant composition is given by the formula

$$C = kI_0 (1 - e^{-\alpha x}).$$

For another mixture of different composition stimulated by the same beam we have

$$C' = k'I_0 (1 - e^{-\alpha' x}),$$

and therefore

$$\frac{C}{C'} = \frac{k (1 - e^{-\alpha x})}{k' (1 - e^{-\alpha' x})},$$

where C and C' are the respective rates of chemical change, and k and α are constants whose magnitudes depend on the composition of the first mixture, and k' and α' are the corresponding constants of the other mixture.

It will be at once perceived that the right hand side of this equation is not, in general, constant, but varies with the value of x . The direct conclusion is that the ratio between the rates of combination in two mixtures of different but definite constitution will depend on the dimensions of the vessel used in the determination. It would appear, therefore, that if Wildermann had employed a vessel of different dimensions, results pointing to a different conclusion would have been obtained. There is only one case in which the amount of light absorbed can be left out of consideration, that is, when the vessel is so large that practically all the actinic rays are absorbed. The light had, however, to pass through only 3.5 cm. of a mixture of carbon monoxide and chlorine, whereas, according to Bunsen and Roscoe, light from a gas flame is reduced in intensity in the ratio of about three to two in passing through 3.5 cm. of pure chlorine under normal conditions. It seems, therefore, that no general statement can be enunciated from such experiments as to the precise effect of the composition of the mixture on the velocity of change.

Conclusions.

(1) No evidence can be obtained of a period of photochemical induction with a moist mixture of chlorine and hydrogen in the absence of impurities which, under the conditions of the experiment, are capable of being destroyed.

(2) The phenomenon hitherto known as photochemical induction is exhibited by a mixture of chlorine and hydrogen to which ammonia or compounds capable of yielding ammonia on decomposition have been added.

(3) The actual compound or compounds which inhibit the inter-

action of chlorine and hydrogen are volatile. They are probably derived from ammonia by the displacement of one or more equivalents of hydrogen by chlorine.

(4) Impure water contains compounds which are very slowly destroyed by chlorine at the ordinary temperature, yielding an inhibitive substance. This fact affords a satisfactory explanation of the phenomenon which has recently been described as "decay of activity."

(5) The inhibitive impurity is of course removed from the system by the influence of light. It can, however, also be destroyed by raising the temperature to 100° . Although stable at the ordinary temperature in a saturated solution of chlorine, it is apparently unstable under the same conditions in a solution which contains very little chlorine.

(6) Sufficient evidence has not, as yet, been adduced to justify us in concluding that condensation nuclei are formed by the action of light on moist chlorine.

(7) The extinction coefficient of a mixture of hydrogen and chlorine in equivalent proportions is almost the same as that of equal volumes of oxygen and chlorine.

It would appear that the following theoretical conclusion can be legitimately drawn from the fact that an induction period cannot be obtained with moist electrolytic gas which is free from destructible impurities. The various phases assumed by an atom of chlorine as it is transformed from a constituent part of a molecule of chlorine to that of a molecule of hydrogen chloride are of a transient and unstable character, the same statement being true about the changes in an atom of hydrogen. Accordingly, neither the chlorine nor the hydrogen atoms can become at any time before their union in hydrogen chloride parts of chemical compounds possessed of a measurable degree of stability. In spite of the fact that we are limited in our choice of theories by the foregoing conclusion, the explanation of the remarkable inhibition effect of minute traces of impurities is still a difficulty. It would appear to be impossible to formulate a consistent hypothesis, free from suppositions which at present are unsupported by experimental results, to account for this phenomenon. The following suggested explanation suffers from this defect and must therefore be regarded as merely provisional.

The light which falls on the moist mixture of chlorine and hydrogen is absorbed in the first instance by the coloured component, namely, the chlorine, and after it has been absorbed it is degraded into heat. During the process of degradation the energy passes through various forms. Now it is conceivable that the distribution of the various kinds of vibration of which the degrading energy is composed will, in certain cases, depend largely on the presence in the system of even small quantities of foreign bodies. A difference in the rate of

chemical change might clearly be expected as the result of a marked difference in the character of the energy through which the light passes as it is transformed into heat. Whether the quality of the energy can vary to the degree required by this hypothesis according as certain impurities are present or not, and whether this variation can be regarded as the chief determining factor of the change, is at present purely a matter of conjecture and awaits experimental confirmation.

THE VICTORIA UNIVERSITY OF MANCHESTER.

CXXXIX.—*Notes on Derivatives of α -N-Alkylated Naphthylamine.*

By RAPHAEL MELDOLA, F.R.S.

THE difficulties encountered in attempting to prepare derivatives of the above type have been pointed out in a paper by the writer and Joseph Henry Lane (Trans., 1904, **85**, 1604). These notes are the outcome of experiments connected with researches on the isomerism of the aminoamidines of the naphthalene series, and are now placed on record as containing descriptions of certain new compounds of the required type which may form useful starting-points in the subsequent extension of the investigations.

Ethyl- α -naphthylamine, being used in the colour industry, can be obtained as a technical product in the form of its very insoluble hydrochloride. A supply of this salt was placed at my disposal by the firm of Leopold Cassella & Co., and was converted into the acetyl derivative by heating with sodium acetate and acetic anhydride. The acetyl derivative crystallises from dilute alcohol in flat, silvery needles melting at 68°.

0.0871 gave 4.9 c.c. moist nitrogen at 14.5° and 770.5 mm. $N = 6.63$.

$C_{14}H_{15}ON$ requires $N = 6.57$ per cent.

It has not been found possible to obtain a mononitro-derivative of ethyl- α -acetylnaphthalide. The compound is nitrated with difficulty and could only be attacked by a mixture of strong sulphuric with fuming nitric acid. The product is a *dinitro*-derivative crystallising from alcohol in small, ochreous needles melting at 221–222°.

0.0913 gave 11.2 c.c. moist nitrogen at 23.2° and 768 mm. $N = 13.94$.

$C_{14}H_{13}O_5N_3$ requires $N = 13.86$ per cent.

Nothing definite could be obtained from this dinitro- α -ethylacet-

naphthalide by oxidation or reduction, and the constitution has therefore not been determined directly. Strikingly characteristic of the compound is the intense violet colouring matter which is produced from it by the action of reducing agents, such as tin and hydrochloric acid, in alcoholic solution. This colouring matter, which is produced only at a transitory stage in the reduction, has not yet been investigated. That one of the nitro-groups is in the para-position (4-homonuclear) is proved by the following synthesis:

1:4-Chloronitronaphthalene, obtained by nitrating α -chloronaphthalene, on heating with an alcoholic solution of ethylamine in a sealed tube to 150° for four hours gives 4-nitro-1-ethylnaphthylamine (*Ch. Fab. Griesheim-Elektron*, D.R.-P. 117006; *Chem. Centr.*, 1901, i, 237). This compound crystallises from glacial acetic acid in orange scales melting at $179\text{--}180^{\circ}$ ($176\text{--}177^{\circ}$ in patent), and on boiling with acetic anhydride for three to four hours is converted into 4-nitro-1-ethylacetnaphthalide, which crystallises from dilute alcohol in small, white needles melting at $112\text{--}113^{\circ}$. The latter, on nitration by dissolving in cold fuming nitric acid, gives the same dinitro-compound (m. p. $221\text{--}222^{\circ}$) as that produced by the direct nitration of ethyl- α -acetnaphthalide.

2:4-Dinitro-1(α)-ethylnaphthylamine.—This compound is easily prepared by the action of ethylamine in alcoholic solution on dinitro- α -naphthol ethyl ether. The latter was obtained by the action of ethyl iodide on the silver salt of dinitro α -naphthol, about 30 per cent. of the dinitro-compound undergoing etherification by this process. An attempt to improve the yield by directly nitrating α -naphthol ethyl-ether under different conditions led to negative results, as a mixture of isomerides is formed instead of the 2:4-dinitro-compound required. On mixing alcoholic solutions of 2:4-dinitro- α -naphthol ethyl ether and ethylamine, interaction takes place at the ordinary temperature, and a crystalline deposit of dinitro- α -ethylnaphthylamine soon separates. This compound crystallises in dense brown prisms with a brilliant lustre, melting at $169\text{--}170^{\circ}$.

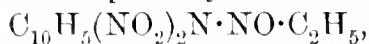
0.1500 gave 20 c.c. moist nitrogen at 12.8° and 768.7 mm. N = 15.93.

0.1331 „ 18.35 „ „ „ „ 12° „ 744.5 „ N = 16.01.

$\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}_3$ requires N = 16.1 per cent.

The substance is practically insoluble in cold alcohol and but very sparingly soluble in boiling alcohol. It can be crystallised from boiling glacial acetic acid or from acetic anhydride. The solutions when allowed to cool rapidly deposit the compound in the form of slender, orange needles. All attempts to prepare an acetyl derivative failed. The substance can be boiled with acetic anhydride and dry sodium acetate for days without undergoing acetylation. Heating with acetic

anhydride in a sealed tube to 170° also failed to yield an acetyl derivative; at higher temperatures, decomposition takes place. A cold acetic acid solution of the compound yields the *nitrosoamine*,



on treatment with sodium nitrite. This compound crystallises from alcohol in transparent, yellow prisms melting at $93-94^\circ$.

0.1257 gave 21.3 c.c. moist nitrogen at 20.7° and 755.7 mm. $\text{N} = 19.18$.

$\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_4$ requires $\text{N} = 19.34$ per cent.

As the acetyl derivative of dinitro- α -ethylnaphthylamine could not be prepared, the corresponding aminoethylamidine could not be obtained. An attempt to reduce the dinitro-compound to ethyltriaminonaphthalene and acetylate the product failed owing to the extremely oxidisable character of the triamino-compound.

4-Bromo-2-nitro-1(α)-benzyl-naphthylamine. — Bromonitro- α -naphthyl ethyl ether (Meldola and Lane, *Trans.*, 1904, **85**, 1605) interacts readily with benzylamine in alcoholic solution, slowly at the ordinary temperature, more rapidly if warmed for a short time on the water-bath. The ethoxy-group is exchanged for the benzylamino-group with the formation of the above compound, which crystallises from alcohol in slender, red needles melting at $126-127^\circ$. The *acetyl* derivative was prepared by heating the substance with acetic anhydride in a sealed tube to 170° for three hours. The crude product was purified by crystallisation from alcohol with animal charcoal and the pure bromonitrobenzyl- α -acetylnaphthalide thus obtained in white prisms melting at 128° .

0.0873 gave 5.15 c.c. moist nitrogen at 12.5° and 766 mm. $\text{N} = 7.05$.

$\text{C}_{19}\text{H}_{15}\text{O}_3\text{N}_2\text{Br}$ requires $\text{N} = 7.02$ per cent.

The bromonitrobenzyl-naphthylamine readily forms a *nitrosoamine* when acted on by sodium nitrite in cold glacial acetic acid solution. This compound crystallises from alcohol in flat, straw-coloured needles melting at 98° .

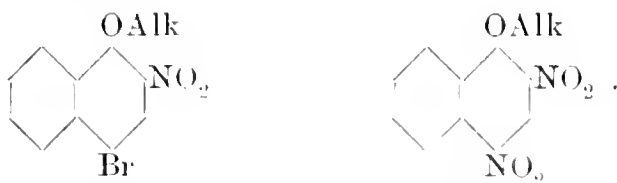
0.0798 gave 7.8 c.c. moist nitrogen at 9° and 761.6 mm. $\text{N} = 10.74$.

$\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_3\text{Br}$ requires $\text{N} = 10.88$ per cent.

The acetyl derivative on reduction by tin and hydrochloric acid gave an anhydro-base which did not appear to be very definite. It is probably a mixture of the bromo-anhydro-base with the benzylamidine, the reducing agent effecting partial debromination. As this benzylamidine offered no advantage over the alkylamidines described in former papers as a means of characterising the isomerides, the investigation of the compound was not further pursued.

The chief point of interest brought out in these notes is the extreme

mobility under certain conditions of the alkyloxy-group in naphthalene derivatives of the types :



The nature of the amine is a determining factor in this interaction, the displacement occurring most readily with alkylamines of the type $R \cdot CH_2 \cdot NH_2$, such as ethylamine and benzylamine. Purely aromatic or hydroaromatic amines such as aniline, α -naphthylamine, and piperidine do not react with the bromonitronaphthyl ether under ordinary conditions. In marked contrast with the readiness with which haloid-nitro- or dinitro-alkylated α -naphthylamine can be formed by the method described in these notes is the apparent impossibility of directly introducing one alkyl group into the haloid-nitro- or -dinitro- α -naphthylamine or the corresponding acetnaphthalides. Many experiments having this object in view were carried out with various alkylating agents under different conditions and invariably with negative results.

CXL.—*Electrolytic Oxidation.*

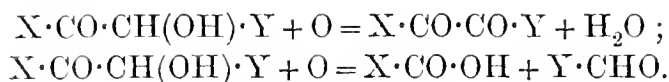
By HERBERT DRAKE LAW, B.Sc.

IN carrying out experiments on the electrolytic oxidation of organic compounds it is advantageous to employ a solvent which mixes with water in all proportions and at the same time does not interfere to any considerable extent with the conductivity of the solution. It must not of course be readily oxidisable. Three classes of compounds suggest themselves, of which acetone, acetic acid, and pyridine may be taken as types. Of these, acetone is by far the most useful, as it can be readily removed by distillation. Pyridine has the characteristics of an unsaturated or aromatic compound, and as a consequence readily forms tarry products which, however, are soluble in water and may be easily removed. It also forms complex soluble tars with other aromatic compounds, which often causes a serious loss of material. In these three solvents the electrolytic oxidation of compounds represented by the general formula

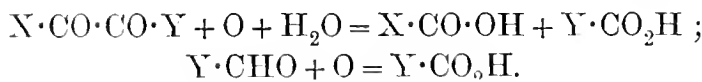


was conducted. Many such compounds are known, of which benzoin is the most important. By changing the groups denoted by X and Y

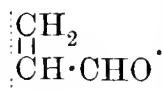
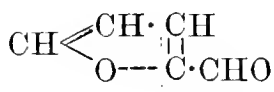
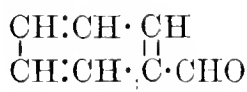
it was hoped to gain a clear idea of the reactions taking place at the anode. Two reactions are possible and may be represented by the following equations :



Two of these products may be oxidised still further according to the equations



Thus, in the case of benzoin the three products obtained, namely, benzil, benzoic acid, and benzaldehyde, are all accounted for in the above equations. When the groups represented by X and Y contain an unsaturated carbon atom, however, a further reaction takes place which cannot be indicated in the form of an equation. Complex resinous substances are formed, the constitution of which is quite unknown. These are extremely interesting, and to gain some knowledge of their mode of formation the oxidation of the unsaturated aliphatic compounds was studied. On comparing the structure of the three aldehydes, namely, benzaldehyde, furfural, and acrolein, a striking similarity of grouping will be seen :



It will be noticed that each compound contains the group
 $\text{—CH}:\text{C}\cdot\text{CHO},$

and as a consequence each might be expected to have some common characteristic. Each of these substances yields complex products at the anode, this being very marked in the cases of furfural and acrolein. That this is due to the unsaturated carbon atoms is borne out by the fact that neither the saturated aliphatic aldehydes nor such saturated ring compounds as camphor possess the same property. It is interesting to note that similar complexes are formed also under the influence of a silent discharge or where a high frequency discharge is used. This again occurs only when unsaturated compounds are employed or are formed during the reaction. It is very probable therefore that a similar phenomenon is taking place at or near the anode, which may be the result of a variable electrical strain set up between the moving molecules and the anode.

The presence of these tars makes the final separation very tedious and the conditions necessary for their formation were studied with a view to their final elimination. The potential of the anode discharge has a very marked effect on their formation, the amount produced

being greatest when the *E.M.F.* reaches the highest value. This is seen very clearly in the cases where the acids sulphuric, hydrochloric, and hydrobromic are used as electrolytes. The potential of discharge of the anions is as follows:

$$\text{SO}_4'' = -0.7 \text{ volt, Cl}' = -0.31, \text{Br}' = +0.06.$$

In sulphuric acid solutions, tarry matter is always formed, but is often absent in the case of hydrochloric acid, and in no case is it formed where hydrobromic acid is employed. Very strong solutions of sulphuric acid also favour the formation of these complex substances, but this is probably a purely chemical reaction and independent of the current.

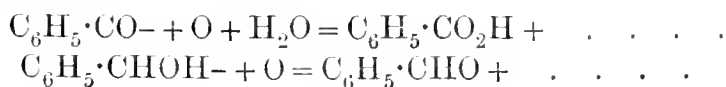
The stability of compounds containing the unsaturated carbon atom is very remarkable. Very little reaction takes place at all when the oxidation is conducted at a low potential, the double link apparently having a retarding influence on the velocity of the oxidation. This protective influence becomes less as the chain is lengthened, the saturated part of the molecule predominating. This retarding action is even greater where a ring compound is introduced. As the potential of the anode is increased, the stability becomes less, and considerable quantities of carbon monoxide are evolved.

This throws a great deal of light on the purely chemical methods of oxidation. The double link is always considered the weakest part of the molecule, and its position is determined by means of such oxidising agents as potassium permanganate. The latter is very vigorous in its action and has, probably, a high oxidation potential which accounts for the decomposition at this point.

Having investigated the mechanism of these reactions, the method was applied to determine the molecular structure of benzfuroin. Two formulæ are possible, represented by (i) and (ii):



The half of the molecule containing the furfurol group most readily decomposes with formation of tarry products, but the remaining part will form benzaldehyde or benzoic acid according to which of the above formulæ is assumed to be correct.



In the actual experiment, benzaldehyde was completely absent, which points to formula (ii) as being correct.

From the compounds anisoïn and piperonyloïn, nothing but tarry matter could be isolated. This might have been due to the difficulty of separating the reaction product, but otherwise this fact shows that

the potential of the complex formation is either lower or very near that of the simple oxidation.

In a paper by James (*J. Amer. Chem. Soc.*, 1899, 21, 889) it was observed that benzoin on oxidation in alcoholic solutions gives a small quantity of benzoic acid, but the chief product was of a tarry nature. If, however, hydrochloric acid was used as an electrolyte a good yield of benzil was obtained and the tar formation was small. This confirms the work of the present paper, that these complex bodies are formed preferably at high potentials.

Benzoin.

The anode compartment consisted of a porous pot of about 400 c.c. capacity, round which was wound a stout platinum wire to serve as cathode. The porous pot was placed in a stout glass jar containing 10 per cent. sulphuric acid to act as electrolyte in the cathode compartment. This in turn was placed in another glass jar containing cold water to keep the whole apparatus cool during each experiment. The porous pot was fitted with a cork bored at the centre, through which a platinum stirrer could be freely rotated. This stirrer, whose superficial area was 37.5 sq. cm., was used also as the anode. In each of the following experiments 15 grams of benzoin were dissolved in the solvent used. In the first five experiments acetone was employed and the benzoin dissolved in 300 c.c. of this substance. Dilute sulphuric acid was then added gradually to this mixture, shaking the whole time, until the total volume measured 375 c.c. In this way most of the benzoin remained in solution. The mixture was then poured into the porous pot and the current started. The oxidised product was invariably dark in colour, due to the formation of some tarry matter. The acetone was then removed by distillation from a water-bath and the non-volatile residue separated. This consisted of a mixture of unchanged benzoin, benzaldehyde, benzil, benzoic acid, and tarry substances. The whole was distilled in steam for several hours. Benzaldehyde rapidly passed over, followed by the benzil, benzoic acid, and a little benzoin. The distillate was made alkaline with sodium carbonate and filtered, the benzil and benzoin remaining on the filter paper. To remove the benzaldehyde, the filtrate was extracted with ether and the ethereal layer dried and evaporated on a water-bath. The remaining solution was acidified with sulphuric acid and the benzoic acid also extracted with ether. The mixture of benzoin and benzil was shaken with a little alcohol to dissolve the benzil, and filtered. In this way these two substances were separated almost completely. The mixture of benzoin and tarry matter in the distilling flask was rendered alkaline with sodium hydroxide and filtered. The

filtrate contained the tar, and the benzoin remained on the filter paper. The tarry matter was again precipitated with dilute sulphuric acid and filtered. In this way most of these substances could be removed from solution, and any small quantity still remaining in solution was extracted with ether. In experiment (6), 300 c.c. of acetic acid were employed instead of acetone. Here the oxidised product was distilled in steam after partial neutralisation of the acetic acid. In this case the ethereal solution of benzoic acid contained also acetic acid, which was removed by careful distillation. In experiment (7), the solvent consisted of 250 grams of pyridine, to which was added 160 c.c. of dilute sulphuric acid. After the oxidation, the product was acidified with sulphuric acid and steam distilled as before. Any pyridine in the distillate was removed from the ethereal solution of benzaldehyde with a little sulphuric acid. The small quantities of benzil obtained in these experiments were mixed together and crystallised once from alcohol. The product melted sharply at 91° , whilst pure benzil melts at 90° . The benzoic acid melted at 121° after being twice recrystallised from alcohol, and was undoubtedly pure. Part of the benzaldehyde was allowed to oxidise in the air to the corresponding acid, which melted at 121° . Another portion was treated with phenylhydrazine and gave a product melting at 154° after being four times recrystallised from alcohol.

TABLE I.

Number of the experiment.	Solvent.	Strength of the acid, per cent.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Benzaldehyde in grams.	Benzil in grams.	Benzoin in grams.	Tar in grams.	Total oxygen absorbed by the benzoin, per cent.
1	Acetone	10	1.0	6	5.5	5.2	4.6	0.5	4.5	1.3	19.6
2	"	10	4.0	6	9.5-10	4.8	3.2	0.5	6.0	1.5	16.8
3	"	30	4.0	6	9.5-10	3.0	1.8	0.5	6.5	5.0	17.6
4	"	3	1.0	6	9.5-10	5.5	3.0	0.5	6.0	1.3	17.2
5	"	10	0.25	6	2.75	5.5	3.7	0.5	4.5	1.0	17.9
6	Acetic acid	10	1.0	6	4.0	2.2	2.2	0.5	10.0	0.5	9.0
7	Pyridine	5	1.0	6	5.0	2.2	1.8	0.25	9.7	0.0	7.9

In Table I the results of seven experiments under varying conditions are given. The last column shows the total amount of oxygen absorbed by the benzoin to form the substances tabulated, the tar being calculated as benzaldehyde. This absorption does not vary much where the same solvent is used, although the products of decomposition do not show the same constant value. The figures of experiment (1) indicate the greatest amount of reaction, and for this reason the conditions used here were adhered to as near as possible in the concluding work. Apparently the tarry colouring matter is most

readily obtained when a large amount of sulphuric acid is present, as is the case in experiment (3). On the other hand, a low current density acts very unfavourably to the formation of this substance, as is seen in number (5). The amount of benzaldehyde and benzoic acid present is greatest where the current density and the concentration of the sulphuric acid are kept low, the former being the most variable. In experiments (6) and (7), different solvents were used. In both cases the total reaction was much less than in the former ones.

In experiment (6), where acetic acid was used as solvent, the percentage amount of benzoin converted into benzaldehyde, benzoic acid, and tar is almost the same as in (1), under the same conditions, but with a different solvent.

The method of obtaining the gaseous products is described later. These experiments gave results agreeing with those conducted with benzaldehyde, and for that reason are not given in detail. Very small amounts of carbon monoxide were formed and even smaller quantities of carbon dioxide. Benzoin is not so soluble as benzaldehyde in acetone, however, and these results are therefore not so accurate as the former, as it is necessary to employ very concentrated solutions.

In the next series of experiments the three products, benzaldehyde, benzoic acid, and benzil, were in turn oxidised and the results tabulated in the following tables.

Benzil.

In these experiments the method of manipulation was exactly the same as in the previous ones. In each case 10 grams of benzil were oxidised and the results are tabulated in Table II. As before, the greatest amount of action was obtained in acetone solutions, whilst in the case of acetic acid this was reduced to half, and to an even smaller amount where pyridine was employed. In each case benzoic acid was produced, accompanied by small quantities of tar, the quantity of the latter being very small in pyridine solutions.

TABLE II.—*Benzil.*

Number of experiment.	Solvent.	Volume of the solvent, per cent.	Strength of the acid, per cent.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Tar in grams.	Unchanged substance in grams.	Amount of oxygen absorbed, per cent.
1	Acetone	66	6·6	1·0	6·0	4·5	7·6	1·3	1·9	14·0
2	Acetic acid	66	6·6	1·0	6·0	6·0	3·5	1·0	4·6	7·1
3	Pyridine	66	6·6	1·0	6·0	9·0	0·4	0·0	8·7	0·7

TABLE III.—*Benzoic Acid.*

1	Acetone	50	5·0	1·0	6·0	3·5	—	1·1	8·9	—
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Only one experiment was conducted with benzoic acid, as the action proceeded very slowly, and the only product formed was a small amount of tarry matter.

TABLE IV.—*Benzaldehyde*.

Number of experiment.	Solvent.	Volume of the solvent, per cent.	Strength of the acid, per cent.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Tar in grams.	Unchanged substance in grams.	Amount of oxygen absorbed, per cent.
1	Acetone	50	5.0	1.0	6.0	4.0	2.1	1.5	2.6	11.3
2	Acetic acid	36	9.6	1.0	6.0	4.0	1.1	0.5	6.3	3.4
3	Pyridine	28	2.8	1.0	6.0	4.5	2.1	0.0	7.0	6.5

The method of manipulation was the same as in the previous cases, benzoic acid and tar being the products. In each case 10 grams of benzaldehyde were oxidised and the results are tabulated in Table IV. The tarry matter was calculated as benzoic acid and the total oxygen is given in the last column. As in the previous cases, the largest amount of reaction took place in acetone solutions, due probably to the small internal friction of the solute. Thus the diffusion of the benzaldehyde into the oxidising layer round the anode will be much greater than in the other experiments. Experiment (3) shows that the activity of the oxidising material is greater in pyridine solution than in those experiments where acetic acid was used. This, however, is contrary to the previous experiments.

In the next series (Table V), the gaseous products obtained on oxidising benzaldehyde electrolytically are given. These were determined in Hofmann's apparatus for the electrolysis of water described in a previous paper (Trans., 1905, 87, 198). In each case two experiments were conducted. In the first a mixture of sulphuric acid and solvent was electrolysed, and then a fresh solution containing a small quantity of benzaldehyde. The gases at the anode consisted of a mixture of carbon dioxide, oxygen, and carbon monoxide, which were analysed in Hempel's bulbs, the differences in each set being due to the decomposition of benzaldehyde. To determine the strength of the current, a gas coulombmeter was coupled in series with the above apparatus. The results were calculated for 500 c.c. of oxygen liberated, and tabulated for comparison. In each case the oxidising surface of the anode was 12.5 sq. dem. These results could never be quantitative where the solvent was readily attacked by the oxygen liberated at the anode, as is the case with acetone and pyridine, for then it is very probable that the introduction of benzaldehyde interferes with the oxidation to a considerable extent. Thus, as the solvent diffuses into the active zone round the anode it is decomposed

by the oxygen available at that point, but when benzaldehyde is present only a part is used in this way, the rest being absorbed by the solute. In this way the amount of some of the gaseous products may be less in the presence of benzaldehyde than when the pure solvent is used. This is seen in the case of pyridine in experiments (3) and (3a), where actually less carbon dioxide is obtained when the aldehyde is present.

TABLE V.—*Benzaldehyde. Gaseous Products.*

Number of experiment.	Solution.	Current in amperes.	E.M.F. in volts.	Pressure in mm. of Hg.	Temperature.	Oxygen liberated in the coulombmeter in c.c.	Total volume of mixed gases in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.	Carbon monoxide in c.c.	Oxygen reacting with the benzaldehyde, per cent.
1	Acetone = 50 % sulphuric acid = 5 %	0.048	6.0	760	17	500	189.4	4.1	134.5	6.2	8.3
1a	Benzaldehyde = 3.3 % conditions as in 1	0.044	6.0	760	17	500	159.4	5.1	102.3	13.7	
Difference between 1 and 1a								1.0	32.2	7.5	
2	Acetic acid = 36 % sulphuric acid = 9.5 %	0.049	4.0	778	16	500	457.0	10.3	421.7	5.1	1.4
2a	Benzaldehyde = 3.5 % conditions as in 2	0.050	4.0	770	16	500	450.0	11.1	418.4	7.1	
Difference between 2 and 2a								0.8	3.3	2.0	
3	Pyridine = 28 % sulphuric acid = 2.8 %	0.059	16.0	757	16	500	218.6	22.3	170.6	6.0	6.5
3a	Benzaldehyde = 2.5 % conditions as in 3	0.059	16.0	760	17	500	187.5	21.9	149.1	9.0	
Difference between 3 and 3a								-0.4	31.5	3.0	

TABLE VI.—*Cuminoin.*

Number of experiment.	Solvent.	Strength of the acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Acid in grams.	Aldehyde in grams.	Unchanged substance in grams.	Tar in grams.
1	Acetone	5 per cent.	1.0	6	4.5	3.5	3.3	2.3	1.0
2	Pyridine	5 ..	1.0	6	10.0	0.5	0.3	8.4	0.0

In experiment (1), ten grams of cuminoin were dissolved in 200 c.c. of acetone, and the whole made up with dilute sulphuric acid to 300 c.c. After the oxidation, the aldehyde was separated by steam distillation,

the acid and unchanged product passing over only very slowly. The latter were separated by means of sodium carbonate, as was also the tar from the unchanged substance in the distilling-flask.

In experiment (2), the amount of pyridine was 200 c.c., made up to 300 c.c. with dilute sulphuric acid. After the oxidation, the pyridine was neutralised with hydrochloric acid, and the whole filtered after standing overnight. The filtrate was extracted with ether and added to the portions already obtained.

The aldehyde and acid were driven off in a current of steam and weighed. As might have been predicted, the oxidation proceeds much in the same way as benzoin, with this difference, however, that cuminoïn appears to be rather more stable than in the former case.

Furoïn.—Ten grams of this substance were dissolved in 150 c.c. of pyridine; 150 c.c. of 10 per cent. sulphuric acid were then added to the solution and the mixture electrolysed. The product was distilled in a current of steam for several hours. Pyridine quickly passed over, followed by bright yellow needles of furil. Sulphuric acid was added to the distillate until it no longer had an odour of pyridine, and the whole was extracted with chloroform. The extract was dried over calcium chloride, and the chloroform evaporated. The residue, after being crystallised once from alcohol, melted sharply at 162° , and was undoubtedly furil. The residue from the steam distillation was acidified, diluted with water, and filtered. The filtrate was extracted with chloroform, and this portion added to the residue on the filter paper. The tar was removed with a solution of sodium carbonate from the unchanged furoïn, and each substance weighed. In this experiment no furfural was detected, and only a trace of furan carboxylic acid was present. The following table gives the details of this experiment:

TABLE VII.

Amount of sulphuric acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Furil in grams.	Tar in grams.	Unchanged furoïn in grams.	Oxygen absorbed.
5 per cent.	1	6	4.5—5.0	3	1.5	3	21.1 per cent.

In order to calculate the total amount of oxygen reacting with the furoïn, the tar was reckoned as furil. This quantity agrees very closely with that obtained in the case of furfural in acetic acid solution. Experiments were also tried with acetone and acetic acid solutions, but in each case the amount of tar was much larger, and for this reason this method was abandoned.

TABLE VIII.—*Benzfuroin*.

Number of experiment.	Solvent	Strength of the acid.	Current in amperes.	Amperes hours.	E.M.F. in volts.	Acid in grams.	Aldehyde in grams.	Benzfural in grams.	Unchanged product in grams.	Tar in grams.
1	Acetone	5 per cent.	1.0	6	3.0	3.2	0.0	0.0	—	2.0

In this experiment, 10 grams of benzfuroin were dissolved in 150 c.c. of acetone, sufficient water and hydrochloric acid were added to make the whole up to 300 c.c., and the mixture subjected to the action of the current as in the previous cases. The acetone was evaporated on a water-bath, and the dark mixture distilled in a current of steam for several hours. In this way a white, crystalline solid was obtained in the receiver. The distillate was made strongly alkaline with sodium hydroxide and filtered, the filtrate acidified with hydrochloric acid and extracted several times with ether. The ethereal extract, on evaporation, yielded benzoic acid, melting at 120° , quite free from any furan derivatives. The part insoluble in alkali was unchanged benzfuroin, and the substance left in the distilling-flask was tar. Similar experiments were conducted in acetone solutions, using sodium hydroxide, sodium sulphate, and sulphuric acid as electrolytes, but in these cases the result was the production of nothing but tarry matter. This was also the case when acetic acid was used as solvent with sulphuric acid as electrolyte.

In pyridine solutions with either lead or platinum anodes, most of the substance was obtained unchanged, but there was invariably a small loss in weight not to be accounted for. The absence of benzaldehyde and benzfural points to the following as being the correct formula for benzfuroin, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_4\text{H}_3\text{O}$, and not $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_4\text{H}_3\text{O}$, for it has been shown that the group $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}-$ is readily oxidised to $\text{C}_6\text{H}_5\cdot\text{CHO}$ and $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}-$, whilst the group $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}(\text{OH})-$ forms tarry products with extreme ease. In all cases where acetone was used as a solvent, except when hydrochloric acid was the electrolyte, very considerable quantities of tarry matter were formed. These were somewhat less when acetic acid was used as a solvent. In pyridine solutions the loss in weight is due to the formation of a tarry substance readily soluble in water, as will be shown in a later part of the paper. In these experiments the potential of the oxidation is evidently too high, and it is only when the *E.M.F.* of the discharged anion is lowered, as in the case of hydrochloric acid, that any substances are formed capable of being identified.

Piperonyloin and Anisoin.

In acetone solutions with either sulphuric or hydrochloric acid as electrolyte, both piperonyloin and anisoin were converted almost completely into dark tarry products. Those obtained from sulphuric acid solutions were completely soluble in sodium hydroxide, and could thus be readily separated from the unchanged product. On acidifying, these were partly reprecipitated in the form of brown, amorphous powders and partly remained in solution. Thus the total product was always less than the amount of substance at the beginning of the experiment. The tarry matter obtained in the case of hydrochloric acid was almost insoluble in sodium hydroxide, and could not, therefore, be separated from the unchanged product. With hydrobromic acid as electrolyte, practically no reaction took place, whilst when pyridine was used the whole of the product remained in solution. In this case the solution obtained when the oxidation was complete was almost black. This was treated with sodium carbonate, and the whole evaporated on a water-bath to dryness. The residue obtained in this way consisted of sodium sulphate, unchanged sodium carbonate, and a dark semi-solid tarry substance. This was shaken up with a small quantity of water, filtered from the sodium salts, and again evaporated to dryness. In this way, 8—9 grams of tar were obtained, a quantity in excess of that taken for the experiment, the excess being supplied by the pyridine itself.

TABLE IX.—*Piperonyloin.*

Number of experiment.	Solvent.	Strength of acid.	Acid used.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Tarry matter in grams.	Unchanged product.
1	Acetone	5 per cent	Sulphuric acid	1.0	3.0	6.0	3.0	1.0
2	"	5 "	Hydrochloric acid	1.0	3.0	13.0	4.5	—
3	"	5 "	Hydrobromic acid	1.0	3.0	5.0	0.1	4.6
4	Pyridine	5 "	Sulphuric acid	1.0	3.0	3.5	—	—

TABLE X.—*Anisoin.*

1	Acetone	5 per cent.	Sulphuric acid	1.0	3.0	6.0	3.0	1.0
2	"	5 "	Hydrochloric acid	1.0	3.0	4.5	1.5	—
3	"	5 "	Hydrobromic acid	1.0	3.0	3.5	0.5	4.5
4	Pyridine	5 "	Sulphuric acid	1.0	3.0	11.0	—	—

Ethyl Benzoin and Benzoin Acetate.

In all the preceding experiments, the group $\text{-CO}\cdot\text{CH(OH)-}$ has remained constant, and the groups attached to the free links only have been altered. These exercise a very important influence on the products of decomposition, and it became of interest, therefore, to determine the action of a substituent in other parts of the molecule. Ethyl benzoin and benzoin acetate are both readily procurable, and were chosen for the experiments. In (1) and (2), ten grams of substance were dissolved in 200 c.c. of acetone, and made up to 300 c.c. with dilute sulphuric acid. After the current had passed for six hours through the mixture, the acetone was removed on a water-bath and the residue distilled in a current of steam. In this way the benzaldehyde passing over was obtained in the first fractions and kept separate. This was followed by benzoic acid and a little unchanged ethyl benzoin or benzoin acetate. These were separated exactly as has been described in previous experiments. It was thought that some product containing the groups $\text{=CH}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ or $\text{=CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ might be formed, but none was discovered, the ethyl and acetyl radicles apparently being eliminated either by hydrolysis or by oxidation during the formation of benzaldehyde. In experiment (3), ten grams of benzoin acetate were dissolved in 200 c.c. of acetic acid, and made up to 300 c.c. with dilute sulphuric acid. After the oxidation, the acetic acid and benzaldehyde were quickly removed by steam distillation and separated as in previous cases. The residue in the flask was made alkaline with sodium hydroxide and filtered when cold. In this way the tar and benzoic acid were removed together. These were precipitated from the alkaline solution with hydrochloric acid and extracted with ether, and the benzoic acid finally obtained by sublimation. It will be seen from these experiments that the course

TABLE XI.—*Ethyl Benzoin.*

Number of experiment.	Solvent.	Strength of the acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Benzaldehyde in grams.	Unchanged substance in grams.	Tar in grams.
1	Acetone	10 per cent.	1.0	6	4.0	3.2	2.2	5.0	0.2

TABLE XII.—*Benzoin Acetate.*

2	Acetone.	10 per cent.	1.0	6	4.5	1.3	2.2	4.6	2.1
3	Acetic acid	5 „	1.0	6	4.5	0.9	0.5	7.0	0.7

of the oxidation is interfered with in no marked manner by the introduction of the ethyl and acetyl radicles into the hydroxyl group. The most noticeable feature is the small amount of tar formed in experiment 1.

Unsaturated Aliphatic Compounds.

Experiment I. Allyl Alcohol.—These experiments were conducted in the same apparatus as in the case of benzoin. Thirty grams of allyl alcohol were made up to 400 c.c. with 10 per cent. sulphuric acid and a current of 1 ampere passed through the solution for twenty-four hours. After a short time an insoluble rubber-like substance was formed, which at the end of the experiment amounted to 2 grams. The mixture was extracted several times with ether and fractionated. Several grams were obtained at 45—65°, consisting of acrolein, and a similar quantity at 65—110°, which was chiefly allyl alcohol. A small amount was obtained above this temperature and the residue charred. The viscid, rubber-like substance was insoluble in water, sodium hydroxide, alcohol, or ether. The fraction above 110° was an acid which decolorised bromine and probably consisted of acrylic acid.

Experiment II.—The same experiment was made with acrolein with the same result.

Experiment III. Crotonaldehyde.—Thirty grams of this substance made up to 300 c.c. were treated as in Experiment I. On the anode there were obtained 2 grams of a viscid substance resembling in all respects that obtained in Experiment I. The ethereal extract on fractionation gave a small quantity of unchanged substance distilling below 150°, and the remainder passed over below 200°, consisting chiefly of crotonic acid. Both these fractions were small. In these experiments the *E.M.F.* was 3.5 volts on commencing, but this rose during the experiment. The anode was the one used in previous cases and measured 37.5 sq. cm.

Unsaturated Compounds.

Gaseous Products.—These experiments were carried out as the previous ones and the results calculated and tabulated for comparison in Table XIII. It will be seen from experiments (2) and (4) that allyl alcohol is by no means readily oxidisable, but is acted on to about the same extent as benzoin in acetone solutions under similar conditions. As the potential increases, however, the stability of this unsaturated compound decreases very considerably, as is seen in experiments (3) and (5), the actual amount of oxygen taking part in these reactions being three times as great. The amount of carbon dioxide liberated remains nearly constant all through, but the carbon monoxide formed increases considerably with the potential. It has been shown by

several authors that the alcohol group decomposes in contact with electrolytic oxygen to form small quantities of carbon dioxide and carbon monoxide (Elbs and Brunner, *Zeit. Elektrochem.*, 1900, **6**, 604), and the same applies to the aldehyde group (*loc. cit.*). These quantities vary very slightly with the potential. The small amount of carbon dioxide liberated in these experiments is due then to the normal decomposition of the alcohol and aldehyde groups, but the large increase in the amount of carbon monoxide is formed by the rupture of the double bond. In experiments (4) and (5) this increase is from 2.7 per cent. to 13.3 per cent. of the total oxidation. This explains the instability of the double linking to ordinary chemical oxidising agents. The potential of the oxygen liberated from such substances as potassium permanganate and nitric acid is very high, and consequently the chain of carbon atoms is attacked at the double bond. The same result is observed in the case of crotonaldehyde, as experiments (6) and (7) show, but not to such a considerable extent. The lengthening of the chain may, however, increase the stability of this substance just as in the case of saturated compounds (*loc. cit.*). Experiments (1) and (8) show the effect of a change in concentration of acrolein. The amounts of carbon dioxide and carbon monoxide are only slightly affected, but the total oxygen reacting is changed very considerably. A comparison of these experiments with corresponding ones conducted with saturated compounds gives very remarkable results. Elbs and Brunner (*loc. cit.*) have shown that in the case of propyl alcohol the amount of oxygen reacting with this substance varies from

TABLE XIII.—*Unsaturated Compounds.*

Number of experiment.	Solution.	Current in amperes.	E.M.F. in volts.	Pressure in mm. of Hg.	Temperature.	Oxygen liberated at the anode in c.c.	Volume of mixed gases in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.	Carbon monoxide in c.c.	Oxygen reacting with the substance, per cent.
1	Acrolein = 8.5 % sulphuric acid = 10 %	0.25	5	750	16°	500	294.1	21.9	243.4	13.5	52.4
2	Allyl alcohol = 5.0 % sulphuric acid = 10 %	0.08	4	764	15	500	442.0	16.0	402.0	13.0	19.6
3	Conditions as in 2	0.30	10	764	13	500	336.4	12.6	273.1	44.2	45.4
4	Allyl alcohol = 15 % conditions as in 2 & 3	0.08	4	760	17	500	454.5	13.5	415.0	13.5	17.0
5	Conditions as in 4	0.31	10	760	17	500	251.5	13.5	174.2	66.9	65.4
6	Crotonaldehyde = 5 % sulphuric acid = 10 %	0.024	4	760	18	500	395.0	10.0	365.0	5.0	27.0
7	Conditions as in 7	0.23	8	760	18	500	378.6	16.5	332.5	14.5	33.6
8	Acrolein = 3 % sulphuric acid = 10 %	0.20	4.5	750	15	500	360.1	16.9	317.0	11.6	34.6

70 to 100 per cent. of the total amount liberated, whilst in the case of allyl alcohol only 20 per cent. is used in the oxidation at low potential. Again, in the case of acrolein, this amount varied from 35 to 50 per cent., whilst propaldehyde reacts with 95 per cent. of the total oxygen (Law, Trans., 1905, 87, 202). Apparently the double bond increases the stability of the rest of the molecule. In these experiments it was noticed that both the anode and the glass became coated with a white, viscous substance.

Furfural.

This substance is undoubtedly an unsaturated aldehyde. For example, it combines readily with bromine, and on oxidation the ring is opened. It behaves in most respects, however, as an aromatic aldehyde, and for this reason these experiments were undertaken. From its general behaviour it ought to fall intermediate between the aromatic and the unsaturated aliphatic aldehydes. Thus the total oxygen reacting with this substance in acetic acid solution is in round numbers 20 per cent., with benzaldehyde 2 per cent., and with acrolein and crotonaldehyde from 30 to 50 per cent. No carbon dioxide and only small quantities of carbon monoxide are liberated in this case, and thus furfural behaves like benzaldehyde. On the other hand, however, the carbon monoxide is doubled on increasing the potential of the decomposition, as in the cases of acrolein and crotonaldehyde. In these experiments, the solvent plays very little part in the reaction, absorbing only from 5 to 15 per cent. of the total oxygen liberated, and the numbers given in Table XIV may therefore be regarded as quantitative. The following table gives the amount of oxygen reacting with four classes of aldehydes.

Benzaldehyde in acetic acid solution. 2 per cent.	Furfural in acetic acid solution. 20 per cent.	Unsaturated aliphatic aldehydes. 30—50 per cent.	Saturated aliphatic aldehydes. 95 per cent.
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Benzaldehyde behaves then as an unsaturated compound, being largely influenced, however, by the stable ring formation of the benzene nucleus. The influence of the ring formation is not so apparent in the case of furfural, and the effect of the unsaturated linking predominates. The unsaturated aldehydes are remarkably stable compounds, and the saturated ones are almost completely decomposed.

TABLE XIV.—*Furfural*.

Number of ex- periment.	Solution.	Current in amperes.	E.M.F. in volts.	Pressure in mm. of Hg.	Temperature.	Oxygen liberated in the coulombmeter in c.c.	Total volume of mixed gases in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.	Carbon monoxide in c.c.	Oxygen reacting with the furfural, per cent.
1	Acetic acid = 16 sulphuric acid = 8	0.053	1	755	17°	500	500.0	0.0	172.7	13.6	19.2
1a	4 grams of furfural, conditions as in 1	0.042	1	754	16	500	431.7	0.0	380.8	18.5	
Difference between 1 and 1a									91.9	4.9	
2	Solution as in 1	0.71	12	754	16°	500	452.0	2.0	420.0	24.0	20.0
2a	Solution as in 1a	0.55	12	754	16	500	363.5	2.1	318.7	32.3	
Difference between 2 and 2a									101.3	8.3	

Menthol and Camphor.

Both these substances are derivatives of six carbon atom ring compounds. They differ from benzene, however, in that they contain no double linking between two carbon atoms. They should therefore form no tarry matter on oxidation, and for this reason the following experiments were undertaken.

Experiment I.—Camphor (10 grams) was dissolved in acetone (20 c.c.) in a beaker, and water and sulphuric acid added until the total volume was 75 c.c., containing 5 per cent. of acid. In this was placed a small porous pot containing 20 per cent. sulphuric acid and a coil of platinum wire to serve as the cathode. The anode was a coil of stout platinum wire 15 cm. long and 1 mm. diameter. A current of one ampere was passed through the solution for twelve hours, at the end of which time the solution in the anode compartment had become slightly yellow, but was apparently free from resinous matter. The acid was partly neutralised with sodium hydroxide and the acetone removed on a water-bath. On cooling, the residue was extracted with ether, dried, and fractionated. The total quantity of product obtained weighed 9 grams, the remainder being lost probably during the experiment. Most of the substance distilled between 200° and 210°, and partly solidified. This was for the most part unchanged camphor. A smaller fraction was obtained below 240°, and there remained in the flask a small oily residue which had darkened somewhat during the distillation. No tarry matter was formed.

Experiment II.—Precisely the same experiment was conducted with

10 grams of menthol. After twelve hours the solution was still quite colourless, and the experiment was allowed to continue overnight. After thirty-six hours the mixture had darkened somewhat, and the experiment was stopped. The product was treated as before and distilled. The bulk of the product which did not solidify was obtained at 200—240°, and there remained behind a small quantity of a dark oily residue. The darkening in this case was entirely due to the accumulation of sulphuric acid in the anode compartment, as was proved in the following experiment. A small quantity of menthol was dissolved in a small quantity of acetone and a few c.c. of 60 per cent. sulphuric acid added. This on standing became brown in a few hours. It was noticed also in the case of benzoin that the presence of large amounts of sulphuric acid favoured the formation of tarry matter. In both these experiments the *E.M.F.* was four volts at the beginning, but towards the end rose considerably owing to the dilution of the acid in the cathode compartment.

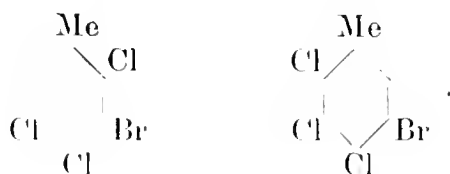
(XLI.—*The Properties of 2:3:4:5-Tetrachlorotoluene.* *A Correction.*

By JULIUS BEREND COHEN and HENRY DRYSDALE DAKIN.

IN a paper on the chlorination of the trichlorotoluenes (Trans., 1904, 85, 1274), it was stated that, whereas 3:4:5-trichlorotoluene was converted on chlorination into a tetrachlorotoluene (m. p. 97—98°), which gave a nitro-derivative melting at 159°, 2:3:4:5-tetrachlorotoluene (prepared from 2:4:5-trichloronitrotoluene by reduction and diazotisation) melted at 86—88°, and gave a nitro-derivative having the same melting point. The conclusion was drawn that, in the former case, seeing that only a 2:3:4:5-tetrachloro-compound could be formed by the chlorine entering the nucleus of 3:4:5-trichlorotoluene, the product which melts at 97—98° must be substituted in the side-chain. It is now found that this view is based on an incorrect observation.

The entrance of chlorine into the side-chain on chlorination in presence of a carrier seemed so unusual a phenomenon that it was thought desirable to examine similar 3:4:5-trihalogen derivatives containing bromine in place of chlorine in order to see if they behaved similarly. With this object, 3:4-dichloro-5-bromotoluene was prepared and was converted into a trichlorobromotoluene in two ways; on the one hand, by successive nitration, reduction, and diazotisation, and on

the other by direct chlorination. In the first case, the product melted at 98–100° and gave a nitro-derivative melting at 171–173°; in the second, the trichlorobromotoluene melted at 92–94° and the nitro-derivative at 175–176°. The two substances are probably isomeric, and represented by the formula



The result of the experiment was to throw grave doubt on the existence of a 2:3:4:5-tetrachlorotoluene (m. p. 86–88°) which yielded a nitro-derivative having an identical melting point.

We consequently prepared 2:3:4:5-tetrachlorotoluene from 3:4:5-trichlorotoluene by nitration, reduction, and diazotisation. The product melted at 97–98° and the nitro-compound at 159°, that is, at the same temperature as the substance produced by chlorinating 3:4:5-trichlorotoluene. Finally, the tetrachloro-compound was prepared from the 2:4:5-trichloro-compound by the method originally adopted. The nitration is easily effected, but the reduction of the nitro-compound is very slow, and a large excess both of tin and strong hydrochloric acid as well as prolonged heating is required. The diazotisation also needs special precautions and must be carried out in presence of strong hydrochloric acid with an excess of sodium nitrite. Under these conditions the base passes into solution and the addition of cuprous chloride precipitates the tetrachloro-compound, which can be filtered and purified by crystallisation. This product also melted at 97–98° and gave a nitro-derivative melting at 159°. Some mistake had therefore been made in the former preparation. On examining the original specimen of 2:3:4:5-tetrachlorotoluene (m. p. 86–88°) it was found to contain nitrogen. There could be no doubt therefore that it was in reality a mixture of tetrachlorotoluene (m. p. 97–98°) and trichloronitrotoluene (m. p. 81°) which had probably escaped reduction. On nitration with fuming nitric acid it appears to have undergone little change, so that the supposed nitro-compound (m. p. 86–88°) was practically the unchanged mixture. This also explains the fact that the analysis of the nitro-compound should have agreed approximately with the theory for the tetrachloronitro-compound (Cl = 51.6), when it is considered that the admixture of tetrachlorotoluene (Cl = 61.7) would raise the percentage of chlorine in the impure trichloronitro-compound (Cl = 44.2). So far the results afford a very simple interpretation. Finally, the action of chlorine on 2:4:5-trichlorotoluene, which was stated to give 2:3:4:5-tetrachlorotoluene

and which was identified by conversion into a nitro-derivative (m. p. 85—86°), has been re-examined.

We pointed out in the former paper the great difficulty experienced in conducting this operation, both in regulating the process and in separating the products. On chlorinating different quantities of material we have been unable to isolate any product except the original substance, which has a remarkable crystallising power, and we have little doubt now that the product which we took to be the 2:3:4:5-tetrachloronitrotoluene (m. p. 86—88°) was in reality the impure nitro-derivative of the original substance, m. p. 91—92°. We have consequently arrived at the following conclusions:

(1) 2:3:4:5-Tetrachlorotoluene melts at 97—98° and gives a nitro-derivative, m. p. 159; (2) there is no other tetrachloro-compound derived from 2:4:5-trichlorotoluene by nitration, reduction, and diazotisation; (3) although by analogy it is very probable that 2:4:5-trichlorotoluene is converted into 2:3:4:5-tetrachlorotoluene on chlorination, we have so far obtained no direct evidence of its formation.

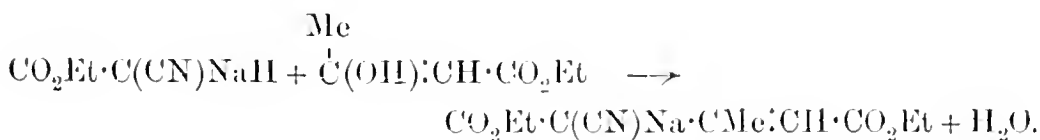
Our thanks are due to Mr. R. S. Horsfall for his help in carrying out some of the experiments.

THE UNIVERSITY,
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CXLII.—*A Method for the Formation of Succinic Acid and of its Alkyl Derivatives.*

By ANNIE HIGSON and JOCELYN FIELD THORPE.

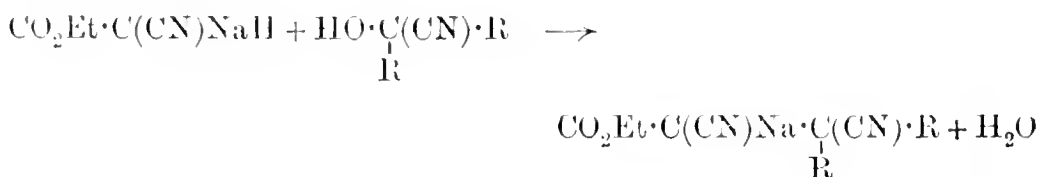
IN a communication dealing with the formation of derivatives of ethyl cyanoglutaconate by the interaction of ethyl cyanoacetate and ethyl acetoacetate (Trans., 1905, **87**, 1685) it was suggested that in all probability this reaction was brought about by the interaction of the mobile hydrogen atom of the sodium derivative with the hydroxyl group of the ketonic ethyl salt in its enolic form, and that in the case of, for example, ethyl- α -cyanoglutaconate, the reaction could be represented by the equation



Since this reaction was subsequently applied to the formation of derivatives of ethyl aconitate by employing ethyl oxalacetate instead

of ethyl acetoacetate in the above synthesis (Trans., 1906, 89, 631), it seemed to us likely to be capable of general application, and in order to decide this point we have investigated the interaction of the sodium compound of ethyl cyanoacetate with various classes of compounds containing the hydroxyl group, and in the present communication deal with the combination of this sodium derivative with a number of typical cyanohydrins.

The condensation between ethyl sodiocyanoacetate and either a ketone- or an aldehyde-cyanohydrin proceeds in nearly all the cases investigated very smoothly at the ordinary temperature; in some instances, especially in those of the aldehyde-cyanohydrins, the reaction is so violent that care has to be taken to cool the reacting products under water. The reaction may be represented by the following general equation:



(R = alkyl or hydrogen).

The condensations were always effected in alcoholic solution and the product isolated by pouring the mixture into water, but since the sodium derivatives formed according to the above equation are not readily dissociated by water it is necessary in every case to render the solution acid before the dicyano-ethyl salt can be isolated. These ethyl salts, which are liquids in the case of the lower members such as, for example, ethyl- $\alpha\beta$ -dicyanopropionate, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, and solids in the case of members higher in the series, such as ethyl- $\alpha\beta$ -dicyano- β -hexylpropionate, $\text{CN}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, and ethyl- $\alpha\beta$ -dicyano- β -phenylpropionate, $\text{CN}\cdot\text{CH}(\text{Ph})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, can be readily extracted and purified either by distillation under diminished pressure or by recrystallisation from some suitable solvent. The alkyl derivatives of succinic acid can then be prepared from these ethyl salts by hydrolysis with hydrochloric acid according to the equation

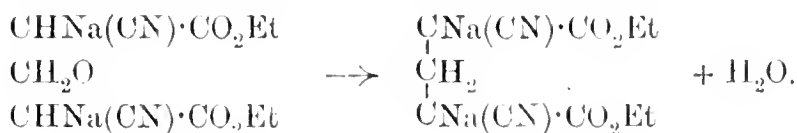


(R = alkyl or hydrogen).

The yields of the condensation products are, in the case of the aldehyde-cyanohydrins, very satisfactory, and are given in a list on page 1459. As regards the ketone-cyanohydrins, special precautions have to be taken in order to avoid the decomposition of the cyanohydrin into the ketone and hydrocyanic acid during the process of the condensation. This is most noticeable in the case of acetone-cyanohydrin, which, as has been observed by A. J. Ultee (*Ber.*, 1906, 39,

1857), is readily decomposed into acetone and hydrocyanic acid in the presence of traces of alkali. However, by employing the conditions described in the experimental portion, a yield in these cases equally as good as that produced in the case of the aldehydecyanohydrins can be obtained.

In the case of formaldehydecyanohydrin, although the reaction partially pursues a normal course when the condensation is effected at low temperatures, yet when conducted in hot solution, and also to a certain extent at the ordinary temperature, ethyl- $\alpha\alpha'$ -dicyanoglutarate, $\text{CN}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, is formed. The production of this substance, which is obtained in large quantities under conditions described in the experimental portion, is evidently due to the decomposition of the cyanohydrin into formaldehyde and hydrocyanic acid and the subsequent condensation of the former with the sodium compound of ethyl cyanoacetate in accordance with the scheme :



The formation of this substance is of interest, because in an attempt to prepare it by the interaction of ethyl cyanoacetate and aqueous formaldehyde in the presence of diethylamine Auwers and Thorpe (*Annalen*, 1895, 285, 322) obtained only complex polymeric compounds of high molecular weight. Ethyl dicyanoglutarate, formed in accordance with the method given in the experimental portion, boils quite constantly at 195° (20 mm.) and is therefore evidently not a polymeride; furthermore, it exhibits no tendency to polymerise under any observed conditions and gives glutaric acid on hydrolysis.

If, however, special precautions are taken to prevent the presence of excess of alkali during the condensation, no trace of the glutaric derivative is formed and the product consists entirely of ethyl- $\alpha\beta$ -dicyanopropionate, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, from which succinic acid can be derived on hydrolysis.

As already mentioned, the first product of the condensation between ethyl sodioeyanoacetate and a cyanohydrin is a sodium derivative of the general formula $\text{CN}\cdot\text{CNa}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CN})\text{R}\cdot\text{R}$, which is stable in the presence of cold water. Therefore the small quantity of water formed in the condensation has no effect on it, and it can be treated directly with an alkyl iodide and give rise to higher alkylated derivatives of succinic acid, thus :



In order to show that this method is of general application we have

applied it to two typical examples, with results which are embodied in the table on page 1459.

The method is not only of value in showing the reactive nature of the remaining hydrogen atom of ethyl sodiocyanoacetate, which has been emphasised in a number of preceding communications, but is also to be recommended as a general method for the preparation of alkyl derivatives of succinic acid. The results obtained are embodied in the table on page 1459.

EXPERIMENTAL.

Condensation of Formaldehydecyanohydrin with the Sodium Compound of Ethyl Cyanoacetate.

As mentioned in the introduction, this condensation may be made to pursue either one of two courses according to the experimental conditions employed. Either the cyanohydrin reacts in the alkaline solution as formaldehyde and condenses with ethyl sodiocyanoacetate, forming ethyl- $\alpha\alpha'$ -dicyanoglutarate,



from which glutaric acid can be derived on hydrolysis, or the cyanohydrin combines directly with the sodium compound, forming ethyl $\alpha\beta$ -dicyanopropionate, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, from which succinic acid can be produced by hydrolysing agents. The first reaction takes place when the heat generated on mixing the condensing substances is unchecked by cooling, the second when the condensation is effected at temperatures below 0° .

In the preliminary experiments, however, it was always found that even at the lower temperature a certain amount of the glutaric derivative was always formed, but it was ultimately observed that by employing the following experimental conditions a pure product could in each case be obtained.

Formation of Ethyl- $\alpha\alpha'$ -dicyanoglutarate,



and Glutaric Acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

Sodium (17.4 grams) was dissolved in absolute alcohol (210 grams) and ethyl cyanoacetate (56.6 grams) added to the solution.

Formaldehydecyanohydrin (15 grams) was then added gradually, the contents of the flask being kept well stirred throughout the addition. The white sodium derivative of ethyl cyanoacetate, which was precipitated on the addition of the ethyl salt to the alcoholic solution of sodium ethylate, instantly dissolved on the addition of the cyanohydrin and considerable heat was at the same time generated. When all the formaldehydecyanohydrin had been added, the contents of the flask con-

Ethyl sodioacetoacetate condensed with the cyanohydrin of	Gives	Yield, Per cent.	Acid formed on hydrolysis.	Sodium derivatives treated directly with methyl iodide * give	Acid formed on hydrolysis.
Formaldehyde :					
Hot	Ethyl- $\alpha\alpha'$ -dicyano-glutarate.	75—80	Glutaric acid.		
Cold	Ethyl- $\alpha\beta$ -dicyanopropionate.	85	Succinic acid.		—
Acetaldehyde	Ethyl- $\alpha\beta$ -dicyano- β -methyl-propionate.	80	Methylsuccinic acid.	Ethyl- $\alpha\beta$ -dicyano- $\alpha\beta$ -dimethylpropionate.	<i>cis</i> - and <i>trans</i> -Dimethylsuccinic acid.
Acetone	Ethyl- $\alpha\beta$ -dicyano- $\beta\beta$ -dimethylpropionate.	65—70	<i>asym.</i> -Dimethylsuccinic acid.	Ethyl- $\alpha\beta$ -dicyano- $\alpha\beta\beta$ -trimethylpropionate.	Trimethylsuccinic acid.
Methyl ethyl ketone	Ethyl- $\alpha\beta$ -dicyano- β -methyl- β -ethylpropionate.	80	$\alpha\alpha$ -Methylethylsuccinic acid.		
Önanthol	Ethyl- $\alpha\beta$ -dicyano- β -hexylpropionate.	95—98	Hexylsuccinic acid.		
Benzaldehyde	Ethyl- $\alpha\beta$ -dicyano- β -phenylpropionate.	95	Phenylsuccinic acid.	—	—

* In each case investigated, the conversion was quantitative.

sisted of a clear, slightly brown, viscid liquid, which, in order to complete the reaction, was allowed to stand at the ordinary temperature for twelve hours.

The condensation product was isolated by pouring the clear solution into a large excess of water and adding hydrochloric acid to the clear solution of the sodium derivative thus obtained. The heavy oil which separated was extracted with ether and the ethereal solution washed first with water and then with a dilute solution of sodium carbonate, dried with calcium chloride, and the ether evaporated. The viscid oil which remained was then fractionally distilled under diminished pressure, when pure ethyl- $\alpha\alpha'$ -dicyanoglutarate was obtained as a clear, strongly refractive liquid boiling at 195° (20 mm.) in yields of about 75–80 per cent.

0.1552 gave 0.3171 CO_2 and 0.0851 H_2O . $\text{C} = 55.72$; $\text{H} = 6.08$.

$\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$ requires $\text{C} = 55.4$; $\text{H} = 5.9$ per cent.

Hydrolysis.—The hydrolysis of the ethyl salt was effected by mixing it with four times its volume of concentrated hydrochloric acid, and heating in a Geissler flask until all oil had passed into solution, an operation which occupied about eight hours ; it was noticed that carbon dioxide was eliminated in considerable quantities during the process. Since the hydrolysed liquid only deposited a small quantity of ammonium chloride on cooling, it was extracted several times with ether, the solution dried over calcium chloride, and the ether evaporated. The gummy residue which remained instantly solidified on scratching, and the solid, after being freed from oil by spreading on a porous plate, was purified by recrystallisation from chloroform, being obtained in large prisms melting at 98° .

0.1799 gave 0.2975 CO_2 and 0.0953 H_2O . $\text{C} = 45.10$; $\text{H} = 5.88$.

$\text{C}_5\text{H}_8\text{O}_4$ requires $\text{C} = 45.4$; $\text{H} = 6.1$ per cent.

The identity of the compound with glutaric acid was shown by its conversion into the anhydride, an operation which was effected by boiling the acid with acetyl chloride until all had passed into solution.

On evaporating the excess of chloride a gum remained which rapidly solidified. Recrystallised from ether it was obtained in slender needles melting at 57° .

Formation of Ethyl- $\alpha\beta$ -dicyanopropionate, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, and Succinic Acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

Besides using quantities of the reacting substances different from those employed in the condensation already described, special precautions were taken in this instance to avoid as far as possible the presence of excess of the sodium derivative of ethyl cyanoacetate or of sodium

ethylate at any time during the progress of the condensation. With this object in view, not only was slightly less than the theoretical quantity of sodium taken in the first instance, but the sodium compound of ethyl cyanoacetate, suspended in the alcoholic solution in which it was precipitated, was added to a well-cooled solution of formaldehydecyanohydrin diluted with alcohol.

The following method was found to give the best results :

5.5 grams of sodium were dissolved in 70 grams of alcohol and 28.3 grams of ethyl cyanoacetate added. The well-cooled alcoholic solution containing the sodium compound in suspension was then added gradually to a solution of 14.3 grams of formaldehydecyanohydrin dissolved in three times its volume of alcohol, care being taken to keep the temperature below 10° throughout the addition. As each addition of sodium compound was made to the cyanohydrin, the insoluble sodium compound instantly dissolved and the temperature rose, necessitating the cooling of the mixture under running water. After all the sodium compound had been added, the clear solution was allowed to stand at the ordinary temperature for two hours, when it was poured into a large excess of water and acidified strongly with hydrochloric acid. On the addition of the acid, a large quantity of oil separated which was extracted with ether, the ethereal solution being washed first with water, then with a dilute solution of sodium carbonate, dried, and the ether evaporated. The oil which remained was then fractionated under reduced pressure, when practically the whole amount distilled constantly at $162\text{--}163^{\circ}$ (20 mm.) as a clear, fairly mobile liquid.

0.2205 gave 0.4459 CO_2 and 0.1099 H_2O . $\text{C} = 55.15$; $\text{H} = 5.52$.

$\text{C}_7\text{H}_8\text{O}_2\text{N}_2$ requires $\text{C} = 55.2$; $\text{H} = 5.3$ per cent.

Hydrolysis.—Ethyl- $\alpha\beta$ -dicyanopropionate was hydrolysed by boiling it with four times its volume of concentrated hydrochloric acid in a Geissler flask until all oil had disappeared. The oil dissolved very rapidly, and after being heated for two hours all had passed into solution, a considerable amount of carbon dioxide being evolved during the process.

The hydrochloric acid solution deposited a quantity of solid on cooling, which was collected and recrystallised from water. The pure acid obtained in this way melted at 187° and possessed all the properties of succinic acid.

0.2202 gave 0.3306 CO_2 and 0.1048 H_2O . $\text{C} = 40.95$; $\text{H} = 5.28$.

$\text{C}_4\text{H}_6\text{O}_4$ requires $\text{C} = 40.7$; $\text{H} = 5.1$ per cent.

The acid was further characterised by converting it into its anhydride by means of acetyl chloride.

Formation of Ethyl- $\alpha\beta$ -dicyano- β -methylpropionate,
 $\text{CN}\cdot\text{CH}(\text{Me})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et},$
and Methylsuccinic Acid, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

This condensation, which proceeds with remarkable readiness, was carried out in the following manner: 5.8 grams of sodium were dissolved in 70 grams of alcohol and 28 grams of ethyl cyanoacetate added to the cooled solution. 17.5 grams of lactic nitrile were then poured in gradually with constant shaking, care being taken to keep the contents of the flask cool by means of running water. On each addition of nitrile, considerable heat was generated, and a portion of the insoluble sodium compound of ethyl cyanoacetate passed into solution. When the requisite quantity had been added all had dissolved, a clear, brown solution being formed. In order to complete the reaction the mixture was allowed to stand at the ordinary temperature for twelve hours, after which time it was poured into water, and the resulting clear solution strongly acidified with hydrochloric acid. On adding the acid, a clear yellow oil separated, which was extracted with ether, the ethereal solution being washed first with water and then three times with dilute sodium carbonate solution and finally evaporated. The residue on distillation under reduced pressure yielded ethyl- $\alpha\beta$ -dicyano- β -methylpropionate as a colourless oil boiling at 160° (20 mm.). The yield represented about 80 per cent. of the amount theoretically possible.

0.2447 gave 0.5180 CO_2 and 0.1254 H_2O . $\text{C} = 57.73$; $\text{H} = 5.76$.

$\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C} = 57.8$; $\text{H} = 6.0$ per cent.

The sodium carbonate washings from the ethereal extract gave some oil on acidifying. This was extracted by means of ether, the ethereal solution dried and evaporated until free from ether, when a viscid oil remained, which decomposed with elimination of carbon dioxide on distillation. Since the compound gave methylsuccinic acid on hydrolysis, there can be little doubt that it was $\alpha\beta$ -dicyano- β -methylpropionic acid, $\text{CN}\cdot\text{CHMe}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$, but the substance exhibited no tendency to become crystalline, and all attempts to induce it to solidify were unsuccessful. The following analysis was made with a specimen which had been dried in an evacuated desiccator for several days.

0.2135 gave 0.4111 CO_2 and 0.0845 H_2O . $\text{C} = 52.51$; $\text{H} = 4.4$.

$\text{C}_6\text{H}_6\text{O}_2\text{N}_2$ requires $\text{C} = 52.2$; $\text{H} = 4.3$ per cent.

The quantity of this acid formed is about 10 per cent. of the theoretical amount. Its formation is evidently due to the inevitable rise of temperature which occurs on the addition of the cyanohydrin, since if the sodium derivative of ethyl cyanoacetate is cooled below 0°

by means of ice and salt, and kept below this temperature throughout the addition of the cyanohydrin, very little of the acid is formed. $\alpha\beta$ -Dicyano- β -methylpropionic acid eliminates carbon dioxide on being slowly distilled under pressure, and a clear, mobile liquid passes over at 253° , which solidifies to a white, crystalline mass when placed in a freezing mixture. It is evidently identical with $\alpha\beta$ -dicyanopropane, prepared by Simpson (*Annalen*, 1862, 121, 160) by the interaction of propylenbromide and alcoholic potash.

Hydrolysis of Ethyl- $\alpha\beta$ -dicyano- β -methylpropionate.—This operation was effected by mixing the ethyl salt with four times its volume of concentrated hydrochloric acid in a Geissler flask and heating the mixture on the sand-bath until all oil had disappeared. During the progress of the hydrolysis, considerable quantities of carbon dioxide were eliminated, and after heating for two hours all the ethyl salt had passed into solution and the evolution of gas had ceased.

The hydrochloric acid liquid was extracted repeatedly by means of ether, the ethereal solution dried with calcium chloride, and the ether evaporated. The gummy residue quickly solidified on scratching, and the acid was purified by recrystallisation from concentrated hydrochloric acid, being thus obtained in needle clusters melting at 112° .

0.1449 gave 0.2420 CO_2 and 0.0800 H_2O . $\text{C} = 45.54$; $\text{H} = 6.18$.

$\text{C}_5\text{H}_8\text{O}_4$ requires $\text{C} = 45.4$; $\text{H} = 6.1$ per cent.

The acid was further identified with methylsuccinic acid by converting it into the anhydride by means of acetyl chloride.

The anhydride crystallised from chloroform in stout prisms melting at 36° (Fichter and Herbrand, *Ber.*, 1896, 29, 1193).

Formation of Ethyl- $\alpha\beta$ -dicyano- $\alpha\beta$ -dimethylpropionate,

$\text{CN}\cdot\text{CHMe}\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$,

and cis- and trans-sym-Dimethylsuccinic Acids,

$\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$.

In this condensation the method adopted was precisely the same as that described in the one above, only after the mixture had stood for the requisite time excess of methyl iodide was added, and the whole gently warmed on the water-bath until a test portion diluted with water gave a neutral reaction towards litmus. When this point had been reached, the product was poured into a large quantity of water, which caused the separation of an oil. This was extracted with ether, the ethereal solution, after being freed from alcohol by washing with water, dried with calcium chloride, and evaporated until free from ether. The residue was a colourless, mobile oil, which, on being

distilled under diminished pressure, was found to boil constantly at 152° (23 mm.).

0.3950 gave 0.8624 CO_2 and 0.2273 H_2O . $\text{C} = 59.58$; $\text{H} = 6.53$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 60.0$; $\text{H} = 6.7$ per cent.

The slightly low values obtained in this analysis are probably due to the presence of traces of unmethylated ethyl salt.

Hydrolysis.—The ethyl salt was hydrolysed in the usual manner, being mixed with about four times its volume of concentrated hydrochloric acid and boiled in a Geissler flask for two hours, when all oil had passed into solution, and the evolution of carbon dioxide, which was apparent during the process of the hydrolysis, had ceased. The hydrochloric acid liquid deposited a considerable quantity of crystals on cooling; these were separated, washed with a little water, and dried.

Without further recrystallisation, the substance melted at 199° , and therefore consisted of nearly pure *trans*-acid. Recrystallised from water, it was obtained in the form of prisms melting at 209° .

0.1645 gave 0.2968 CO_2 and 0.1001 H_2O . $\text{C} = 49.10$; $\text{H} = 6.75$.

$\text{C}_6\text{H}_{10}\text{O}_4$ requires $\text{C} = 49.3$; $\text{H} = 6.9$ per cent.

This acid was identified as *trans*-dimethylsuccinic acid by converting it into the anhydride, which was effected by means of acetyl chloride. It melted at 43° (compare Bone and Perkin, *Trans.*, 1896, 69, 266).

In order to isolate the *cis*-acid, the hydrochloric acid mother liquors were evaporated to dryness, the dried solid extracted with ether, and the ethereal solution, after being dried with calcium chloride, evaporated until free from ether. The residual gum, which solidified on scratching, was then rubbed with a little cold water, filtered from a small quantity of *trans*-acid which remained undissolved, and the clear filtrate mixed with an equal volume of concentrated hydrochloric acid. On standing, crystals of the *cis*-acid slowly separated and were found to melt at 129° .

0.1996 gave 0.3605 CO_2 and 0.1286 H_2O . $\text{C} = 49.26$; $\text{H} = 7.04$.

$\text{C}_6\text{H}_{10}\text{O}_4$ requires $\text{C} = 49.3$; $\text{H} = 6.9$ per cent.

The acid was characterised as *cis*-dimethylsuccinic acid by converting it into its anhydride (m. p. 87°) by means of acetyl chloride. A careful examination of the mother liquors failed to reveal any trace of methylsuccinic acid, and therefore apparently the conversion of the sodium compound into the methyl derivative by direct treatment with methyl iodide is practically complete under the experimental conditions described.

Formation of Ethyl- α -dicyano- β -dimethylpropionate,
 $\text{CN}\cdot\text{CMe}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et},$
and asym-Dimethylsuccinic Acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

Some little difficulty was, in the first instance, experienced in determining the right conditions under which the condensation of acetonecyanohydrin with the sodium compound of ethyl cyanoacetate could be effected.

When the condensation was carried out in the same way as that already described in the case of lactic nitrile, it was observed that a very considerable reduction in temperature took place on adding the cyanohydrin to the sodium compound, and that the yield of the condensation product scarcely exceeded 20 per cent. of the theoretical amount. This reduction in temperature is evidently due to the decomposition of acetonecyanohydrin into acetone and hydrocyanic acid in the presence of the alkaline sodium compound, or of traces of free sodium ethylate mixed with it. It has been recently shown by A. J. Ultee (*Ber.*, 1906, **39**, 1857) that traces of alkali bring about this decomposition and that heat is absorbed during the process. Recourse was therefore had to the method adopted in the case of the condensation of formaldehydecyanohydrin and ethyl sodioacyanoacetate, in which, in order to avoid excess of the sodium derivative at any time during the condensation, it was added gradually to a solution of the cyanohydrin in absolute alcohol, and at the same time slightly less than the theoretical amount of the sodium was taken. In this way, a yield representing about 65—70 per cent. of the theory was obtained.

Sodium (5.5 grams; theory requires 5.8 grams) was dissolved in absolute alcohol (70 grams), and ethyl cyanoacetate (28 grams) added. This mixture, after being well cooled, was then added gradually to a solution of 22 grams of acetonecyanohydrin dissolved in an equal volume of alcohol, the contents of the flask being vigorously shaken after each addition. It was noticed that during this process the temperature rose appreciably, and that the sodium derivative of ethyl cyanoacetate slowly passed into solution.

When all had been added, the mixture was allowed to stand for an hour, when the contents of the flask were found to have become solid owing to the separation of the sodium compound of the condensation product. A large excess of water was then added, and the resulting clear solution made faintly acid with hydrochloric acid. The addition of the acid caused the separation of an oil, which, however, was found again to pass into solution on the addition of a large excess of acid. In this, therefore, and in the other experiments, care was always taken not to add an excess of acid. The precipitated oil was extracted by means of ether, the ethereal solution washed with water and dilute

sodium carbonate solution, dried with calcium chloride, and the ether evaporated. The residual oil, on distilling under diminished pressure, was found to consist almost entirely of ethyl- $\alpha\beta$ -dicyano- $\beta\beta$ -dimethylpropionate, which is a colourless, fairly mobile liquid boiling at 150° (22 mm.).

0.1798 gave 0.3970 CO_2 and 0.1131 H_2O . $\text{C} = 60.23$; $\text{H} = 6.98$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 60.0$; $\text{H} = 6.7$ per cent.

Hydrolysis.—The ethyl salt was mixed with four times its volume of concentrated hydrochloric acid and the mixture heated in a Geissler flask for three hours. The oil dissolved very quickly in the strong acid solution, and the evolution of carbon dioxide became very vigorous as soon as the solution began to boil. The hydrolysed liquid deposited a considerable quantity of crystalline substance on cooling. This was separated and recrystallised from water, *asym*-dimethylsuccinic acid being thus obtained in large prisms melting at 139° .

0.1798 gave 0.3227 CO_2 and 0.1102 H_2O . $\text{C} = 48.94$; $\text{H} = 6.87$.

$\text{C}_6\text{H}_{10}\text{O}_4$ requires $\text{C} = 49.3$; $\text{H} = 6.9$ per cent.

The acid was further characterised by converting it into its anhydride by means of acetyl chloride. Recrystallised from benzene it showed the correct melting point, namely, 29° .

Formation of Ethyl- $\alpha\beta$ -dicyano- $\alpha\beta\beta$ -trimethylpropionate,
 $\text{CN}\cdot\text{CMe}_2\cdot\text{CMe}(\text{CN})\cdot\text{CO}_2\text{Et}$,
and Trimethylsuccinic Acid, $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$.

In the condensation of acetonecyanohydrin and ethyl sodioacyanoacetate described above, it was mentioned that after the mixture had been allowed to stand for one hour the contents of the flask became solid owing to the separation of the sodium compound of the condensation product. In the present experiment, excess of methyl iodide was added directly to the sodium derivative prepared in this way and the whole gently warmed on the water-bath until a test portion on dilution with water gave a neutral reaction to litmus. Water was then added, and the oil which was precipitated extracted by means of ether. The ethereal solution, after being washed with water to free it from alcohol, was dried with calcium chloride and evaporated until free from ether. The residual oil on being distilled under diminished pressure gave ethyl- $\alpha\beta$ -dicyano- $\alpha\beta\beta$ -trimethylpropionate as a clear, colourless oil boiling at 150° (20 mm.).

0.1554 gave 0.3409 CO_2 and 0.1003 H_2O . $\text{C} = 61.58$; $\text{H} = 7.15$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 61.9$; $\text{H} = 7.2$ per cent.

The yield of the pure ethyl salt is about the same as in the case of the corresponding dimethyl derivative, being about 70 per cent. of the theoretical amount.

Hydrolysis.—The ethyl salt was hydrolysed in the usual way, being mixed with four times its volume of concentrated hydrochloric acid and heated on the sand-bath until all oil had dissolved, a process which took nearly six hours. On cooling, the hydrolysed liquid deposited a considerable quantity of crystalline acid, which was collected and recrystallised from water, being thus obtained in colourless prisms melting at 152° .

0.2258 gave 0.4338 CO_2 and 0.1524 H_2O . $\text{C} = 52.39$; $\text{H} = 7.5$.

$\text{C}_7\text{H}_{12}\text{O}_4$ requires $\text{C} = 52.5$; $\text{H} = 7.5$ per cent.

The acid was further identified as trimethylsuccinic acid by converting it into its anhydride. This compound was found to possess the correct melting point, namely, 38° .

An examination of the mother liquors failed to reveal any trace of *asym*-dimethylsuccinic acid, and therefore the conversion of the sodium derivative into the methyl compound is practically complete under the experimental conditions described.

Formation of Ethyl- $\alpha\beta$ -dicyano- β -methyl- β -ethylpropionate,
 $\text{CN} \cdot \text{CMeEt} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$,
and α -Methyl- α -ethylsuccinic Acid, $\text{CMeEt}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

Although methylethylketonecyanohydrin behaves in much the same way as acetonecyanohydrin, that is to say, when treated with the alkaline sodium derivative, a certain amount of heat is absorbed, yet it was found that when the cyanohydrin was added slowly to the sodium derivative in alcohol very little change in temperature occurred, and that after the mixture had stood for half an hour the temperature slowly began to rise. The following method was found to give a yield of the condensation product representing about 80 per cent. of that theoretically possible.

5.6 grams of sodium (slightly less than a quarter molecule) were dissolved in 70 grams of alcohol and 28 grams of ethyl cyanoacetate added; 25 grams of methylethylketonecyanohydrin were then introduced in small quantities at a time. A slight absorption of heat was noticed, but apparently little change occurred, since the white sodium compound of ethyl cyanoacetate remained unaltered. The mixture was allowed to stand at the ordinary temperature for twelve hours. After standing for half an hour it was noticed that heat was being generated, and that the sodium derivative was gradually passing into solution. The flask was therefore cooled under running water and

again allowed to stand, this process being repeated as often as any appreciable rise in temperature took place. After standing the requisite time, the contents of the flask consisted of a thick, yellow mass. Water was added, and the clear, yellow solution rendered acid by means of hydrochloric acid. The yellow oil which then separated was extracted with ether, the ethereal solution washed with water and then with dilute sodium carbonate solution, dried with calcium chloride, and the ether evaporated. The residual oil, on distilling under diminished pressure, was found to consist of pure ethyl- $\alpha\beta$ -dicyano- β -methyl- β -ethylpropionate, a colourless oil boiling at 162° (20 mm.).

0.1352 gave 0.3165 CO_2 and 0.0855 H_2O . $\text{C} = 63.84$; $\text{H} = 7.01$.

$\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 64.1$; $\text{H} = 6.8$ per cent.

The sodium carbonate washings from the ethereal extract gave only a trace of oil on acidifying, showing that very little of the dicyano-acid was formed during the condensation.

Hydrolysis.—The ethyl salt was hydrolysed by boiling it in a Geissler flask with four times its volume of concentrated hydrochloric acid until all oil had passed into solution and until the evolution of carbon dioxide had ceased, a process which took about four hours. Since the hydrolysed liquid did not deposit any crystalline substance on cooling, it was extracted several times with ether, and the ethereal solution, after being dried over calcium chloride, evaporated until free from ether. The gum which remained instantly solidified on scratching, and the solid acid was purified by dissolving it in water, adding an equal volume of concentrated hydrochloric acid, and allowing the solution to stand. Fern-like needles slowly separated which melted sharply at 104° .

0.1698 gave 0.3251 CO_2 and 0.1164 H_2O . $\text{C} = 52.23$; $\text{H} = 7.60$.

$\text{C}_7\text{H}_{12}\text{O}_4$ requires $\text{C} = 52.5$; $\text{H} = 7.5$ per cent.

The acid was characterised by converting it into its anhydride by means of acetyl chloride. The acid was boiled with the chloride until all had passed into solution, when the excess of chloride was evaporated in an evacuated desiccator over potash. Since the anhydride showed no signs of solidifying it was distilled under diminished pressure, when a colourless, mobile liquid passed over at 140° (20 mm.), which showed no signs of crystallising after standing some weeks. According to Hell (*Ber.*, 1891, 24, 1393) and Auwers and Fritzweiler (*Annalen*, 1896, 289, 170), the anhydride of this acid is a liquid.

Formation of Ethyl- $\alpha\beta$ -dicyano- β -hexylpropionate,
 $\text{CN}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et},$
and Hexylsuccinic Acid, $\text{CH}(\text{C}_6\text{H}_{13})(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

The condensation between α -nantholecyanohydrin and the sodium derivative of ethyl cyanoacetate proceeds very smoothly, and the yield of the condensation product is practically quantitative. The method adopted was as follows : 5.8 grams of sodium were dissolved in 70 grams of alcohol, and the solution mixed with 28 grams of ethyl cyanoacetate ; 35 grams of α -nantholecyanohydrin were then added in small quantities at a time. After each addition, heat was generated, and the mixture had to be cooled under running water. When all had been added, the whole of the sodium compound had passed into solution and a clear, yellow liquid remained, although in order to complete the reaction the mixture was allowed to stand twelve hours at the ordinary temperature. Water was then added, and the solution acidified with hydrochloric acid. On the addition of the acid, a yellow oil separated which was extracted with ether, the ethereal solution being washed first with water to free it from alcohol, then with dilute sodium carbonate solution, and finally dried over calcium chloride. The solution was then evaporated until free from ether and the residual oil distilled under diminished pressure, when the pure ethyl salt passed over as a viscid, colourless oil at 192° (20 mm.), which solidified on standing to a white, crystalline cake. Recrystallised from dilute methyl alcohol, it was obtained in large prisms which melted at 45° .

0.1598 gave 0.3869 CO_2 and 0.1279 H_2O . C = 66.03 ; H = 8.85.

$\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_2$ requires C = 66.1 ; H = 8.5 per cent.

The sodium carbonate washings from the ethereal solution deposited a small quantity of oil on acidifying which gradually became solid. When recrystallised from methyl alcohol it was obtained in small needles which melted at 97° . The quantity, however, was too small for analysis, although, since it gave off carbon dioxide on heating at 180° , there can be no doubt that it was $\alpha\beta$ -dicyano- β -hexylpropionic acid, $\text{CN}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$.

Hydrolysis of Ethyl- $\alpha\beta$ -dicyano- β -hexylpropionate.—This hydrolysis was effected in the usual way, namely, the ethyl salt was mixed with four times its volume of concentrated hydrochloric acid and heated on the sand-bath for eighteen hours. The fact that the hexylsuccinic acid which is formed during the process of the hydrolysis is insoluble in concentrated hydrochloric acid renders it a matter of some difficulty to determine the end-point of the hydrolysis. It was found, however,

that it was finished when the evolution of carbon dioxide, which was abundant at the commencement, had ceased, and when a test portion of the oil completely dissolved on treatment with sodium carbonate solution. The oil which floated on the surface of acid liquid after the hydrolysis had been effected solidified on cooling. It was separated and recrystallised from dilute alcohol, being obtained in small plates melting at 87° .

0.1300 gave 0.2844 CO_2 and 0.1082 H_2O . $\text{C} = 59.66$. $\text{H} = 9.24$.

$\text{C}_{10}\text{H}_{18}\text{O}_4$ requires $\text{C} = 59.4$; $\text{H} = 8.9$ per cent.

Hexylsuccinic acid is readily soluble in hot water, but sparingly so in cold. It is difficult, however, to recrystallise it from this solvent, since, owing to its low melting point, it frequently separates as an oil. The best method was found to be as follows: the acid was dissolved in boiling water, and, after cooling, a few drops of methyl alcohol were added to the solution in order to redissolve any oil which may have been precipitated. This solution on standing deposited the acid slowly in glistening plates. When first prepared, the acid has an odour resembling a fatty acid, but it lost this on recrystallisation and was then quite odourless.

The *silver* salt was prepared by adding a solution of the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid. The white precipitate which then separated was collected and dried.

0.2573 gave 0.1424 Ag. $\text{Ag} = 51.72$.

$\text{C}_{10}\text{H}_{16}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 51.80$ per cent.

The *anhydride*, $\begin{array}{c} \text{CH}(\text{C}_6\text{H}_{13}) \cdot \text{CO} \\ | \\ \text{CH}_2 \text{---} \text{CO} \end{array} \text{>O}$, was prepared by boiling the acid with acetyl chloride until all had passed into solution and until the evolution of hydrogen chloride had ceased. After the excess of chloride had been evaporated in an evacuated desiccator over potash, the gum which was left quickly solidified. The anhydride thus formed crystallised from light petroleum (b. p. $60\text{--}80^{\circ}$) in slender, long, colourless needles melting at 57° .

0.1351 gave 0.3231 CO_2 and 0.1098 H_2O . $\text{C} = 65.22$; $\text{H} = 9.02$.

$\text{C}_{19}\text{H}_{16}\text{O}_3$ requires $\text{C} = 65.2$; $\text{H} = 8.8$ per cent.

The anhydride dissolved on boiling with water, and on cooling hexylsuccinic acid melting at 87° separated from the solution.

The *anilic acid*, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}(\text{C}_6\text{H}_{13}) \cdot \text{CO} \cdot \text{NHPh}$, was formed by adding a benzene solution of the anhydride to a solution of freshly-distilled aniline in the same solvent. The mixture became at once hot and then almost solid owing to the separation of the anilic acid. It

was purified by recrystallisation from benzene and in this way obtained in microscopic plates melting at 122° .

0.1149 gave 0.2927 CO_2 and 0.0847 H_2O . $\text{C} = 69.48$; $\text{H} = 8.18$.

$\text{C}_{16}\text{H}_{23}\text{O}_3\text{N}$ requires $\text{C} = 69.3$; $\text{H} = 8.3$ per cent.

Formation of Ethyl- $\alpha\beta$ -dicyano- β -phenylpropionate,
 $\text{CN}\cdot\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$,
and Phenylsuccinic Acid, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

The condensation between the sodium compound of ethyl cyanoacetate and mandelic nitrile also gave good results, and the yield in this case as well as in the one above was almost quantitative. The method adopted was as follows: 5.8 grams of sodium were dissolved in 70 grams of alcohol and 28 grams of ethyl cyanoacetate added. Thirty-three grams of mandelic nitrile were then added to the alcoholic solution containing the insoluble sodium compound in suspension, in small quantities at a time. Considerable heat was generated after each addition, and it was found necessary to regulate the temperature by cooling under running water. When all the nitrile had been added, the sodium compound had passed into solution and the clear, brown liquid which was formed was allowed to stand twelve hours in order to complete the reaction. After this time the product was poured into water and the solution rendered acid by means of hydrochloric acid. The oil, which was then precipitated, was extracted by means of ether, the ethereal solution washed several times with water to remove alcohol, then thoroughly with a dilute solution of sodium carbonate, and, after drying over calcium chloride, evaporated until free from ether. The viscid, brown oil which remained became solid on standing. It was spread on a porous plate to remove oily impurities, and then recrystallised from dilute methyl alcohol. The ethyl salt was thus obtained in colourless plates melting at 64° .

0.1952 gave 0.4920 CO_2 and 0.0954 H_2O . $\text{C} = 68.71$; $\text{H} = 5.47$.

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 68.4$; $\text{H} = 5.3$ per cent.

The sodium carbonate washings from the ethereal solution gave an oil on acidifying which rapidly solidified. It was collected by filtration and recrystallised from dilute alcohol, being obtained in colourless plates melting at 72° . This compound, which is soluble in sodium carbonate solution, gave the following results on analysis:

I. 0.1447 gave 0.3750 CO_2 and 0.0787 H_2O . $\text{C} = 70.67$; $\text{H} = 6.04$.

II. 0.1254 gave 0.3250 CO_2 and 0.0697 H_2O . $\text{C} = 70.69$; $\text{H} = 6.23$.

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 70.9$; $\text{H} = 6.4$ per cent.

From these figures it is apparent that the substance is not the free

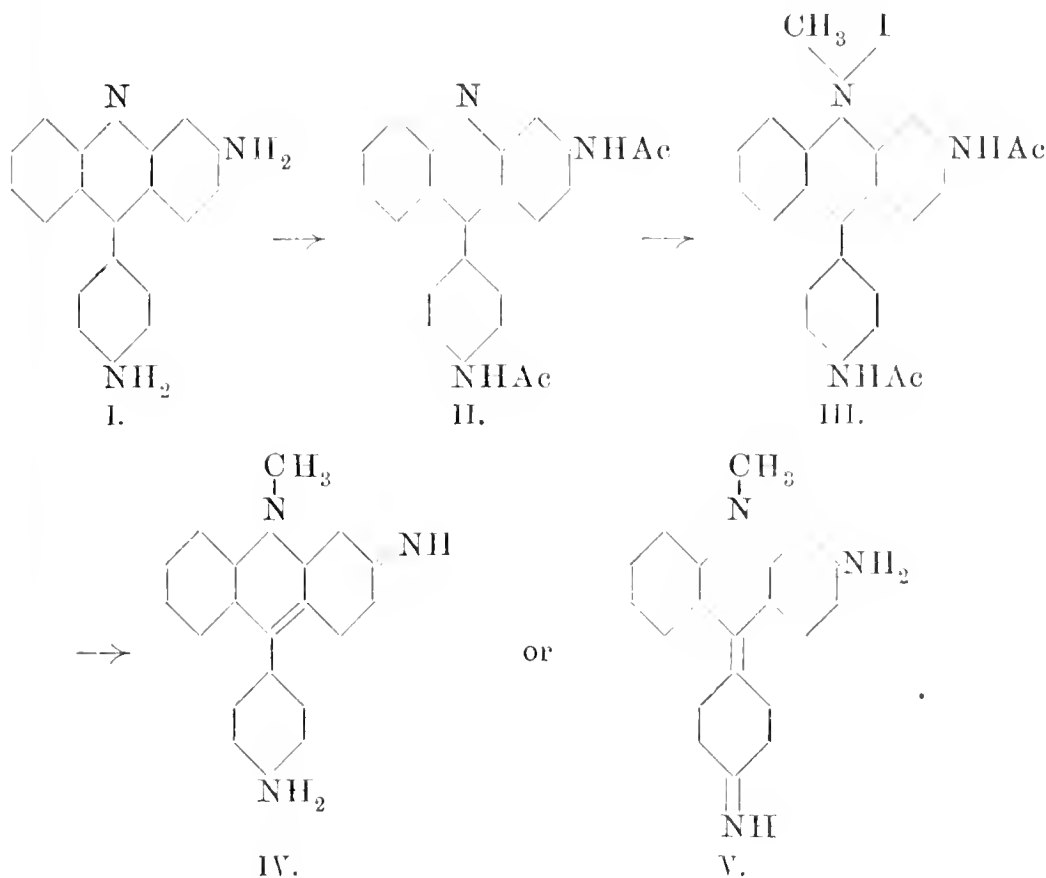
acid (namely, $\alpha\beta$ -dicyano- β -phenylpropionic acid), and it is difficult to say what the constitution of the body can be, since the quantity formed was too small for an extended investigation. The fact, however, that on hydrolysis with hydrochloric acid it was converted into phenylsuccinic acid shows that it must be closely related to the true condensation product in constitution.

Hydrolysis.—Ethyl- $\alpha\beta$ -dicyano- β -phenylpropionate was hydrolysed in the same way as in the case of the previous ethyl salts described, being mixed with four times its volume of concentrated hydrochloric acid and heated on the sand-bath until a test portion was completely soluble in sodium carbonate solution, a process which required from two to three hours. On cooling, the hydrolysed liquid became partially solid owing to the separation of the acid. The solid was separated by filtration and recrystallised from hot water, when phenylsuccinic acid was obtained in warty aggregates melting at 168° .

0.1499 gave 0.3408 CO_2 and 0.0746 H_2O . $\text{C} = 62.01$; $\text{H} = 5.5$.

$\text{C}_{10}\text{H}_{10}\text{O}_4$ requires $\text{C} = 61.8$; $\text{H} = 5.2$ per cent.

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It will be noted that the product of the hydrolysis of diacetylchrysanthemidine methiodide with boiling dilute sulphuric acid and precipitation with caustic soda has been represented by either of two alternative formulæ, IV and V, of which the authors prefer the latter.

Fischer and Körner in their research on chrysanthemidine (*Ber.*, 1884, 17, 203; *Annalen*, 1886, 226, 175) mention that Claus had observed the smooth exchange of an amino- for a hydroxy-group by heating with fuming hydrochloric acid for several hours at 160°; the resulting chrysophenol was further examined by the authors mentioned, who prepared an acetyl derivative and a platinichloride. We considered that the addition of methyl iodide to the acetyl derivative of chrysophenol would be of interest, not merely on account of the possibility of obtaining a new anhydro-base, but also as being likely to furnish further information respecting the colour and fluorescence of acridine derivatives in relation to their constitution.

The chrysophenol used in this investigation was prepared in a manner similar to that indicated by Claus, the acid used was probably somewhat weaker ("pure hydrochloric"), and the time, ten hours, longer. The preparation of sufficient material was very tedious, but good yields were obtained. The tubes were frequently almost filled with deep garnet-coloured needles, apparently quite homogeneous, and

not melting below 250° ; these appear, however, to consist of mixed crystals of the hydrochloride and sal-ammoniac. An air-dried specimen, submitted to no further purification, gave the following analytical results:

0.1399 gave 15.2 c.c. dry nitrogen at 29° and 756 mm. $N = 12.3$.

0.2120 gave 0.1463 AgCl. $Cl = 17.1$.

$C_{19}H_{14}ON_2 \cdot HCl \cdot NH_4Cl$ requires $N = 11.2$; $Cl = 18.8$ per cent.

The fact that a small amount of the chrysaniline remains unattacked would explain the discrepancy between the calculated and found percentages. Claus and Fischer and Körner regarded the crystalline substance from their tubes as being a mixture of sal-ammoniac and chrysophenol hydrochloride, but did not note the apparent homogeneity and uniformly acicular character of the crystals.

The free base was obtained from the crystals after separation of the mother liquor by solution in water and addition of alkali. A trace of unchanged chrysaniline was precipitated and removed by filtration, and the chrysophenol separated from the alkaline solution as a salmon-coloured, flocculent mass by exact neutralisation with dilute acid.

When prepared in this way, chrysophenol is a red substance which darkens considerably on drying. It is slightly soluble in water and freely so in alcohol or acetone, but is dissolved far less readily by ether or benzene. For purification it was dissolved in hot alcohol, water added until a slight turbidity was produced, the solution again heated, and then allowed to cool. Small, maroon needles were thus obtained, which melted at 115° to a clear liquid and gave the following results on analysis:

0.0693 gave 6.5 c.c. dry nitrogen at 30° and 754 mm. $N = 10.5$.

$C_{19}H_{14}ON_2$ requires $N = 9.8$ per cent.

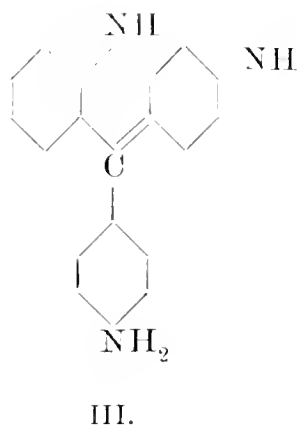
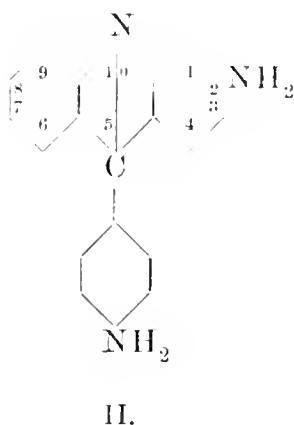
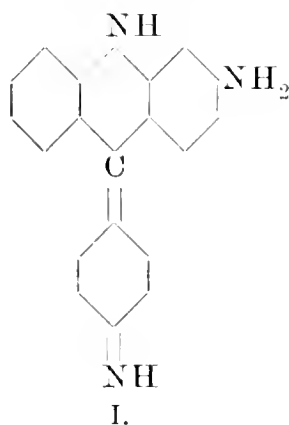
Chrysophenol dissolves in concentrated sulphuric acid with strong deep green fluorescence, the fluorescence exhibited by chrysaniline under these conditions being similar but less intense. On dilution, the chrysophenol fluorescence persists, whilst that of chrysaniline disappears.

The solution of chrysophenol in alcohol does not exhibit fluorescence, but chrysaniline and benzoflavine both give fluorescent solutions in this solvent, especially the latter diamino-base, which is more symmetrical.

In order to obtain an idea as to the cause of these phenomena, it is desirable to know which amino-group in chrysaniline is displaced in its conversion to chrysophenol. We are of opinion that it is undoubtedly the amino-group in position 2 and not that in position 5-*p* which is eliminated. Phenylacridine when nitrated or chlorinated

yields di-substitution derivatives with such ease as to suggest that two symmetrical positions are attacked (A. E. Dunstan and R. O'F. Oakley, *Ber.*, 1906, **39**, 981), and it is scarcely probable that these would be in the 5-phenyl nucleus which is attached to the *meso*-carbon atom. Since there is always the possibility of quinonoid structure between this *meso*-carbon atom and positions 2 and 8, the latter seem to be the likely points of attack, a view which receives support from analogous reactions in the azine and oxazine series. The displacement of amino-groups in positions 2 and 8 in the acridine nucleus by hydroxyl under the influence of acids has been patented by L. Cassella and Co. (D.R.-P. 121686) and further studied by F. Ullmann and R. Fitzenkam in the case of acridine yellow (*Ber.*, 1905, **38**, 3794), so that we have no hesitation in ascribing to chrysophenol the constitution of 2-hydroxy-5-*p*-aminophenylacridine.

The fully symmetrical benzoflavine may be expected to fluoresce strongly in alcoholic solution, and this is the actual case. If, corresponding to the scheme given in our last communication on p. 488, we endeavour to represent chrysaniline tautomerically, we see that three formulæ are possible :



Formulæ I and III, although very similar, are not identical, and the fluorescence of this compound, as mentioned, is not so marked as that of benzoflavine.

If we construct corresponding formulæ for chrysophenol (where the NH in position 2 is replaced by O), we see that the structures corresponding to I and III are not very similar, in fact we should hardly expect the molecules to swing regularly between the extreme configurations. It has already been stated that chrysophenol in alcoholic solution does not fluoresce, a result in good agreement with the theoretical deduction.

Although chrysophenol contains a phenolic group and is soluble in alkali, yet it is a base of considerable strength. Fischer and Körner prepared two series of salts from it, indicating that it may behave as

a di- or mono-acidic base. We have further characterised the substance by the preparation of a chromate and a platinichloride.

Chrysophenol chromate, obtained by adding potassium chromate to a solution of the hydrochloride, is a sandy-yellow, crystalline powder not melting below 250° . After washing with alcohol and drying in a vacuum, the following result was obtained on analysis:

0.1321 gave 0.0251 Cr_2O_3 . $\text{Cr} = 12.5$.

$\text{C}_{19}\text{H}_{14}\text{ON}_2 \cdot \text{H}_2\text{CrO}_4$ requires $\text{Cr} = 12.8$ per cent.

Chrysophenol platinichloride was precipitated by addition of hydrogen platinichloride to the aqueous solution of the hydrochloride as a brown, sandy powder. The salt was analysed after washing with alcohol and drying in a vacuum:

0.2097 gave 0.0420 Pt. $\text{Pt} = 20.0$.

$(\text{C}_{19}\text{H}_{14}\text{ON}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 19.8$ per cent.

The nitrate of chrysophenol gives a double salt with silver nitrate (whitish-yellow precipitate); the salts of chrysophenol also furnish yellow precipitates with phosphomolybdic acid and potassium ferrocyanide.

Acetylation of Chrysophenol.

A diacetyl derivative of chrysophenol is obtained on boiling a mixture of the base with its own weight of fused sodium acetate and five times its weight of acetic anhydride for some hours in a reflux apparatus. The change of colour to the brownish-yellow of the acetylated product is significant, though not so marked as in the case of chrysaniline. The contents of the flask were poured into weak alcohol to destroy excess of acetic anhydride, and semi-crystalline crusts appeared on cooling, which, after recrystallisation from glacial acetic acid, formed dark brown needles. This substance does not melt below 250° , dissolves in strong sulphuric acid with vivid greenish-blue fluorescence, and, from its analysis, appears to be the *acetate* of *diacetylchrysophenol*.

0.2480 gave 0.6275 CO_2 and 0.1236 H_2O . $\text{C} = 69.0$; $\text{H} = 5.5$.

$\text{C}_{25}\text{H}_{22}\text{O}_5\text{N}_2$ requires $\text{C} = 69.7$; $\text{H} = 5.1$ per cent.

The bulk of the alcoholic solution obtained after acetylation was neutralised with dilute ammonia with production of a flocculent, orange-coloured precipitate. This was collected, washed, dried, and recrystallised from absolute alcohol, in which it is fairly soluble. After drying at 100° , analysis showed that the substance was *diacetylchrysophenol*.

0.0590 gave 0.1610 CO_2 and 0.0307 H_2O . $\text{C} = 74.4$; $\text{H} = 5.8$.

0.3208 gave 21.2 c.c. dry nitrogen at 27° and 761 mm. $\text{N} = 7.6$.

$\text{C}_{23}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{C} = 74.6$; $\text{H} = 5.4$; $\text{N} = 7.5$ per cent.

Diacetylchrysophenol does not melt below 250° , and its alcoholic solution exhibits no fluorescence. The substance possesses basic character, as shown by the isolation of the acetate; a chromate and a platinichloride have also been prepared.

Diacetylchrysophenol chromate, obtained by the addition of potassium chromate solution to a solution of the base in dilute alcoholic hydrochloric acid, is a yellow, crystalline precipitate. Washed with alcohol and dried in a vacuum, the substance was found not to melt below 250° , and gave the following result on analysis:

0.1044 gave 0.0113 Cr_2O_3 . $\text{Cr} = 6.31$.

$(\text{C}_{23}\text{H}_{18}\text{O}_3\text{N}_2)_2\text{H}_2\text{CrO}_4$ requires $\text{Cr} = 6.04$ per cent.

Diacetylchrysophenol platinichloride was prepared by adding hydrogen platinichloride to a warm solution of the base in alcoholic hydrochloric acid. It is a brownish-yellow, crystalline powder which, after washing with alcohol and drying in a vacuum, was analysed:

0.1901 gave 0.0310 Pt. $\text{Pt} = 16.3$.

$(\text{C}_{23}\text{H}_{18}\text{O}_3\text{N}_2)_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 16.8$ per cent.

Benzoylation of Chrysophenol.

On benzoylating chrysophenol in caustic soda solution, according to the Schotten-Baumann method, a non-crystalline product was obtained. The alcoholic solution, when poured into water, yielded a yellow, gummy mass; when, however, the alcoholic solution was poured into a strong solution of potassium chromate, a bright yellow, flocculent precipitate was formed, which, washed with alcohol and dried in a vacuum, gave results agreeing with the composition of a *chromate of dibenzoylchrysophenol*.

0.1133 gave 0.0080 Cr_2O_3 . $\text{Cr} = 4.8$.

$(\text{C}_{33}\text{H}_{24}\text{O}_3\text{N}_2)_2\text{H}_2\text{Cr}_2\text{O}_4$ requires $\text{Cr} = 4.7$ per cent.

Action of Dimethyl Sulphate on Diacetylchrysophenol.

A mixture of diacetylchrysophenol and considerable excess of dimethyl sulphate was gradually warmed to nearly the boiling point in a reflux apparatus, the heating being continued for two hours. A striking colour change occurred, the beautiful brilliant green fluorescence first produced gradually disappearing and the melt assuming a magnificent crimson shade. After cooling, the mass was dissolved in

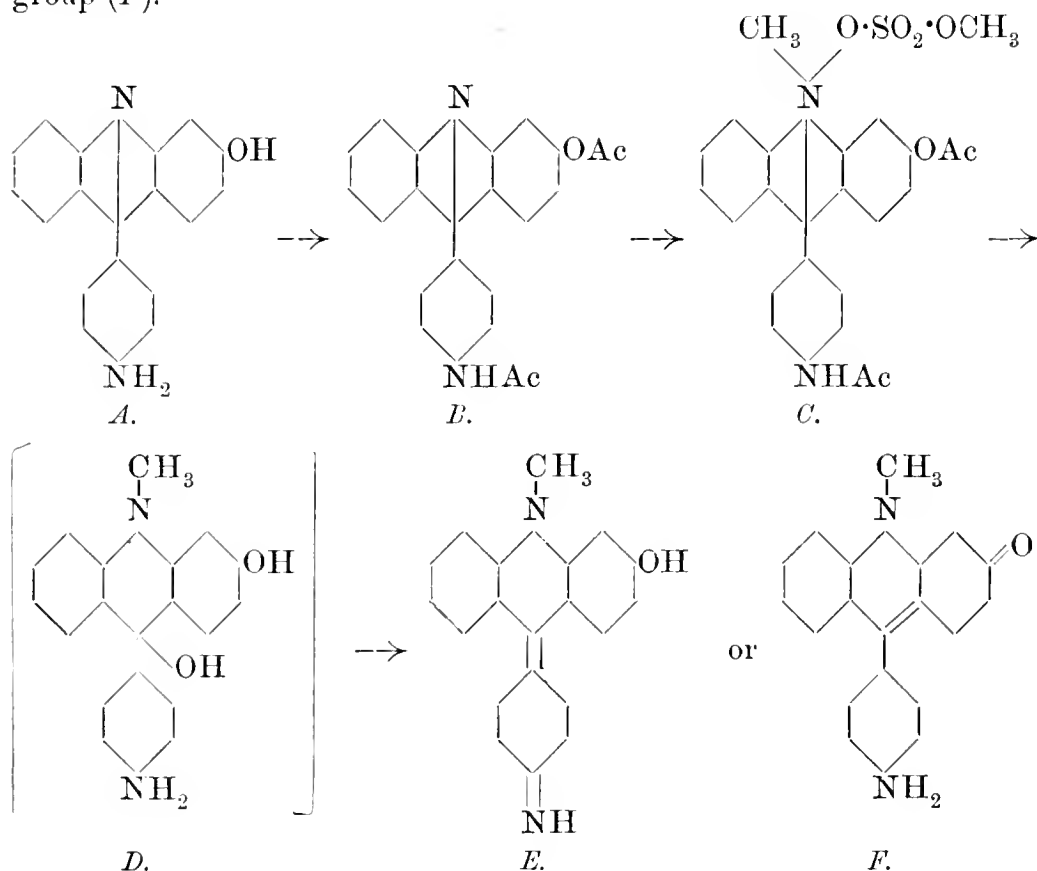
hot water and boiled for one hour with an equal bulk of 4*N*-sulphuric acid. On exact neutralisation of the fine red solution, a brown, flocculent precipitate was produced; this proved to be soluble not only in excess of acid but also of alkali. The substance, after collection, washing, and drying, was nearly black; by extraction with boiling alcohol, addition of water, and slow evaporation, a deep red, crystalline deposit was formed, which, after drying at 100°, gave the following results on analysis:

0.1140 gave 0.3312 CO₂ and 0.0550 H₂O. C = 79.2; H = 5.36.

0.1089 „ 9.6 c.c. dry nitrogen at 27° and 761 mm. N = 9.9.

C₂₀H₁₆ON₂ requires C = 80.0; H = 5.33; N = 9.33 per cent.

The analytical numbers point to an *anhydro*-base, the initial solubility of the substance in alkali indicates the probability of the substance being first precipitated as a carbinol base, the subsequent elimination of water taking place either with the amino-group (*L*) or the hydroxyl group (*F*).



The new anhydro-base is insoluble in ether, fairly soluble in acetone or alcohol; its deep red solutions show no trace of fluorescence.

Hydrochloride.—The term “hydrochloride” is a misnomer; the dark red salt formed on concentration of a solution of the anhydro-base in dilute hydrochloric acid is formed by addition of equimolecular

proportions of the two constituents without elimination of water, but has the constitution of a quaternary ammonium compound. The ring is so stable that to obtain satisfactory results by the Carius method a temperature of nearly 300° was necessary.

0.1549 gave 0.0701 AgCl. Cl = 10.5.

$C_{20}H_{16}ON_2Cl$ requires Cl = 10.6 per cent.

Platinichloride.—This yellow, crystalline precipitate was analysed :

0.0605 gave 0.0119 Pt. Pt = 19.6.

$(C_{20}H_{16}ON_2)_2H_2PtCl_6$ requires Pt = 19.3 per cent.

Dichromate.—A dichromate is obtained on addition of potassium chromate solution to the chloride; it is also a yellow, crystalline precipitate.

0.1085 gave 0.0203 Cr_2O_3 . Cr = 12.8

$(C_{20}H_{16}ON_2)_2H_2Cr_2O_7$ requires Cr = 12.8 per cent.

In conclusion we desire to express our thanks to Mr. R. O'F. Oakley for most useful assistance.

EAST HAM TECHNICAL COLLEGE.

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CXLIV.—*The Relation of Position Isomerism to Optical Activity. VII. The Rotation of the Menthyl Esters of Three Isomeric Dinitrobenzoic Acids.*

By JULIUS BEREND COHEN and HENRY PERCY ARMES.

THE menthyl esters which were selected for investigation were those of the 2:4-, 2:6-, and 3:5-dinitrobenzoic acids, which were prepared from the corresponding acid chlorides by heating them with menthol in the manner described in former papers.

The following are the constants of the compounds in question :

	M. p. of acid chloride.	M. p. of ester.	In benzene solution.	
			$[\alpha]_D^{20}$.	$[M]_D^{20}$.
2 : 4.....	42—46°	69—71°	—134°	—470°
2 : 6.....	96—98	121—123	—183	—642
3 : 5.....	66—68	153—154	—70	—246

In a previous communication on this subject (Trans., 1905, 87, 1190), it was shown that, of the three mono-nitro-esters, the ortho-compound produced the greatest effect in increasing the laevorotation

and the para- the least, whilst the meta-compound occupied an intermediate position. The present experimental results fully confirm our former observations. The di-ortho-compound exhibits the highest and the di-meta- the lowest rotation of the three esters examined, whilst the compound which contains one nitro-group in the ortho- and one in the para-position has a constant which is nearly the mean of the other two. Attention should be drawn to the interesting fact that the rotation of the di-meta-compound is very little different from that of the unsubstituted benzoic ester.

Although similar observations have been made before, the large rotational effect of the nitro-group in the ortho-position renders the present result more striking. The results of the study of the seven isomeric series of substituted benzoic esters which have been laid before the Society furnish abundant evidence that it is only the substituent near the active group which materially influences its activity. The only apparent anomaly is presented by the three iodobenzoic esters. Unfortunately, the difficulty of preparing other isomeric series of substituted benzoic acids containing iodine renders the optical study of their esters very troublesome.

EXPERIMENTAL.

Menthyl 2:4-Dinitrobenzoate.—The 2:4-dinitrobenzoic acid which served for these experiments was obtained from Kahlbaum. It was converted into the acid chloride in the usual way by heating it with an equal weight of phosphorus pentachloride on the water-bath. After removal of the oxychloride by distillation under diminished pressure, the solid residue was crystallised from light petroleum. It forms colourless needles (m. p. 42—46°). The action of the acid chloride on menthol began at 140°, and when the process was completed the product was made alkaline and distilled in steam to remove any free menthol. The ester was crystallised from alcohol and melted at 69—71°. The following are the polarimetric observations in benzene solution at different concentrations:

Concentration, per cent.	Rotation.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
31.148	− 81.48°	− 130.79°	− 458.16°
15.57	− 42.00	− 134.84	− 472.34
7.78	− 21.37	− 137.21	− 480.65

Mean of $[M]_D^{20}$ − 470°.

On analysis:

0.3104 gave 21.5 c.c. moist nitrogen at 15° and 750.5 mm. N = 8.05.

$C_{17}H_{22}O_6N_2$ requires N = 8.0 per cent.

Menthyl 2:6-Dinitrobenzoate.—The preparation of 2:6-dinitro-

benzoic acid in any quantity is a very troublesome operation. After several trials, the method which was adopted was to heat 2:6-dinitrotoluene in sealed tubes for twelve hours at 125—130° with nitric acid, consisting of 2 volumes of strong acid of sp. gr. 1.4 and 1 volume of water. On account of the large quantity of gas liberated during oxidation, it is necessary to release the pressure occasionally by opening the tubes. The yield is always very poor and the crude acid very much discoloured. The product melted at 198—203°, and, after repeated crystallisation from water with the addition of charcoal, was obtained colourless and melted at 201—203°. Fourteen grams of dinitrotoluene gave about 3 grams of impure acid. The small yield necessitated frequent repetitions of the process in order to obtain the requisite quantity of material. The acid chloride was prepared by the usual method, and after crystallisation from light petroleum melted at 96—98°. On heating the latter with menthol in the oil-bath, the reaction began very slowly, and was completed in two and a half hours at 150—160°. The treatment of the product was the same as described in the case of the 2:4-ester. The crude ester was very dark-coloured and required frequent crystallisation from alcohol with the addition of charcoal to produce a pure substance. It crystallises in prisms, m. p. 121—123°.

The polarimetric readings in benzene solution were as follows:

Concentration, per cent.	Rotation.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
14.104	-51.75°	-183.4°	642.5°
7.052	-25.76	-182.7	640.0
3.526	-12.96	-183.9	644.2

Mean of $[M]_D^{20^\circ}$ = 642°.

On analysis:

0.2557 gave 18.8 c.c. moist nitrogen at 18° and 751 mm. $N = 8.45$

$C_{17}H_{22}O_6N_2$ requires $N = 8.0$ per cent.

Menthyl 3:5-Dinitrobenzoate.—The acid was obtained from Kahlbaum, and was converted into the acid chloride in the usual way. After crystallisation from light petroleum it melted at 66—68°. The interaction of the acid chloride and menthol began at 100°, and became very vigorous at 110°. The process was completed in ten minutes, when the contents of the flask solidified. The ester crystallised from alcohol in colourless needles, m. p. 153—154°.

The polarimetric readings in benzene solution were as follows:

Concentration, per cent.	Rotation.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
9.612	-13.47°	-70.08°	-245.6°
4.806	-6.74	-70.15	-245.8
2.403	-3.40	-70.76	-247.9

Mean of $[M]_D^{20^\circ}$ = 246°.

On analysis :

0.3038 gave 21.9 c.c. moist nitrogen at 16° and 744.5 mm. $N = 8.28$.

$C_{17}H_{22}O_6N_2$ requires $N = 8.0$ per cent.

APPENDIX.—By JULIUS BEREND COHEN.

Steric Hindrance in the Interaction of Menthol with Diortho-substituted Benzoyl Chlorides.

The following observations have been made incidentally during the preparation of a series of isomeric disubstituted benzoic esters of menthol by my co-workers and myself, and are now collected together with the object of furnishing a contribution to the theory of "steric hindrance." Sudborough (Trans., 1895, 67, 587) has shown that diortho-substituted benzoyl chlorides are more slowly hydrolysed than the corresponding isomerides. In reference to the action of alcohols, he points out that "in order to obtain the (ethereal) salts of the diortho-substituted acids it is necessary to boil the acid chlorides for some time with the alcohol, as the action seems to proceed more gradually."

No actual examples are quoted, but the methyl esters of 2:4-, 3:5-, and 2:6-dibromobenzoic acids and 2:6-dinitrobenzoic acid are described as being readily obtained from the acid chlorides and methyl alcohol.

A more definite indication of steric hindrance was apparently derived from the behaviour of 2:4:6-tribromobenzoyl chloride and 2:4:6-trinitrobenzoyl chloride, the methyl ester of the first being obtained by boiling the chloride "for some time" with methyl alcohol, and that of the second by boiling the chloride "with a very large excess of methyl alcohol for some time," whilst methyl alcohol appeared to leave 2:3:4:6-tetrabromobenzoyl chloride to a great extent unaltered. On the other hand, the methyl ester of 3:4:5-tribromobenzoic acid was prepared by boiling the chloride with methyl alcohol "for a few minutes." It will be seen that the examples are not very numerous, and that the indications of steric hindrance are not always of a very pronounced character.

During the last few years, six separate series of isomeric disubstituted benzoic esters of menthol have been prepared for optical examination by the interaction of the acid chlorides and menthol (Trans., 1903, 83, 1214; 1904, 85, 1265; 1906, 89, 49, 460). The series comprise 6 isomeric dichloro- and dibromo-benzoic esters, 10 chlorobromobenzoic esters, 8 chloronitrobenzoic esters, and 3 dinitrobenzoic esters. In all, 33 disubstituted benzoyl chlorides have been transformed into corresponding menthyl esters.

It is impossible to determine with accuracy the temperature at which the reaction between the acid chloride and alcohol commences, but by carefully watching the surface of the liquid and the outlet tube of the flask in which the process is going forward there is no difficulty in ascertaining within a very few degrees the visible indication of its commencement. Bubbles begin to rise in rapid succession from the body of the liquid, and fumes of hydrogen chloride escape.

As a rule the reaction, when once a definite temperature is reached, proceeds vigorously; but in the case of the diortho-substituted acid chloride it is invariably retarded. Briggs and the author (*Trans.*, 1903, 83, 1214) noticed that "evidence of steric hindrance is very clearly indicated in the case of the 2:6-dichlorobenzoic acid, for whereas the acid chlorides, as a rule, react vigorously with menthol at 135—140°, no reaction occurs with 2:6-dichlorobenzoyl chloride until the temperature reaches 180°, and even then it proceeds very slowly." A similar observation was made by Zortman and the author (*Trans.*, 1906, 89, 49), who found that "as in former examples of diortho-acid chlorides the 2:6-dibromobenzoyl chloride required a much higher temperature for esterification (175—180°) than the isomeric acid chlorides, all of which react rapidly below 130° with menthol." In another paper by Raper and the author (*Trans.*, 1904, 85, 1265) it is stated "that the 2:6-chlorobromobenzoyl chloride, like the corresponding dichlorobenzoyl chloride, does not react with menthol until a temperature of 180° is reached." In other cases the reaction was completed at 130—140° or below. In preparing the chloronitrobenzoic esters described by Armes and the author (*Trans.*, 1906, 89, 460) it was found that "the reaction (of the 2:6-acid chloride) with menthol does not begin until the temperature reaches 150°, and then proceeds very slowly at 150—160°." In other cases the reaction was completed at 120°; in that of the 3-chloro-5-nitro-compound at 95—100°. Armes and the author also find in the case of the dinitrobenzoic esters that whereas interaction with 2:6-dinitrobenzoyl chloride and menthol begins at 150° and proceeds very slowly, that with the 2:4-compounds begins at 140° and is rapidly completed, whilst with the 3:5-compound the reaction set in at 100° and was completed in a few minutes at 110°.

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CXLV.—*Optically Active Reduced Naphthoic Acids.*
Part III. The Relative Catalytic Effect of Bases
on the Compounds of Δ^2 -Dihydro-1-naphthoic Acid.

By ROBERT HOWSON PICKARD and JOSEPH YATES.

It has been shown in Part I (Trans., 1905, 87, 1767) that the transformation of the sodium salt of *d*- Δ^2 -dihydro-1-naphthoic acid to the corresponding salt of the inactive Δ^1 -acid is easily followed by polarimetric observations, and proceeds in the presence of sodium hydroxide as a unimolecular reaction. An alteration in the concentration of the sodium hydroxide, or its replacement by another base, causes an alteration in the velocity of the change, and thus the transformation affords a method of comparing the strength of bases as regards this particular reaction.

The molecular rotatory power of the sodium salt in 1.3 to 1.5 per cent. aqueous solution is approximately the same as that of the potassium salt, and it is probable that each is fairly completely ionised at this concentration.

The first series of experiments was carried out with this concentration of the sodium salt at 30° in solutions of varying concentrations of different bases. The velocity of the transformation is approximately proportional to the hydroxyl ions, but is probably changed slightly in some cases by an alteration in the state of ionisation of the optically active reagent.

Thus the velocity constant, $K = \frac{1}{t} \log \frac{C_o}{C_t}$, obtained in *N*/4 sodium hydroxide, was 0.0225, whilst in *N*/10 sodium hydroxide the value obtained was 0.00749, whereas if the velocity of the transformation were proportional to the concentration of hydroxyl ions, the value in the second case should be slightly greater than 2/5ths of 0.0225, since these solutions of sodium hydroxide are almost completely ionised. But if we compare two solutions, which contain different concentrations of hydroxyl ions, but the same concentration of sodium ions, the velocity constants are then proportional to the concentration of the hydroxyl ions. Thus the velocity constant of the transformation when carried out in *N*/4 sodium hydroxide + *N*/4 sodium chloride is 0.0234, and when carried out in *N*/10 sodium hydroxide + 4*N*/10 sodium chloride is 0.00931.

The following table of results shows that as regards the catalytic effect on the transformation of sodium $\Delta^{2(\text{or } 3)}$ -dihydro-1-naphthoate the hydroxides of the alkali metals are somewhat weaker than those of the alkaline earths, but are slightly stronger than the tetra-alkyl

ammonium hydroxides. The relative strength of the bases as measured by the results obtained differ somewhat from the relative electrical conductivity of the same. This we attribute mainly to the effect of the base on the degree of ionisation of the sodium salt. In this connection it may be pointed out that the alteration in the value of the velocity constant with varying concentrations of the base is proportionally the same in the case of solutions of potassium and barium hydroxides, which, according to their electrical conductivities, are ionised to approximately the same extent.

Concentration of hydroxide.

	<i>N</i> /2.	<i>N</i> /4.	<i>N</i> /5.	<i>N</i> /10.	<i>N</i> /20.	<i>N</i> /25.
Sodium hydroxide... ..	0·0530	0·0225	—	0·00749	—	—
Potassium „	0·0550	0·0239	0·0179	0·00769	—	—
Lithium „	—	0·0257	—	—	—	—
Calcium „ .. .	—	—	—	—	—	0·00468
Strontium „	—	—	—	0·0121	0·00467	—
Barium „	—	0·0362	0·0277	0·0113	0·00528	0·00364
Tetramethylammonium hydroxide	—	0·0181	—	—	—	—
Tetraethylammonium hydroxide	—	0·0210	—	—	—	—
Tetra- <i>n</i> -propylammonium hydroxide	—	0·0141	—	—	—	—

A point of some interest is that the velocity of the transformation of the *d*-sodium salt is identical with that of the *l*-sodium salt; thus, in *N*/10 strontium hydroxide the velocity constant of the transformation of the *l*-salt is 0·0118, whilst that of the *d*-salt is 0·0121. These results are almost identical, and represent the usual divergence of duplicate experiments, which is not greater than 3 per cent.

Some experiments made with dilute alcoholic solutions of sodium hydroxide show that the velocity constants are greater in these solutions than in water. Here, however, this is possibly due not only to the influence of the alcohol on the degree of ionisation of the optically active salt, but also to the influence of the medium. The influence of concentration of the sodium salt on the velocity of the transformation is proportionally the same in 50 per cent. alcohol as in water, whilst in solutions of varying alcoholic strength and the same concentration of sodium hydroxide the velocity constants increase rapidly in value as the concentration of the water decreases.

Sodium chloride exerts an accelerating influence on the rate of transformation in the presence of sodium hydroxide, as will be seen from the following table:

In *N*/4 NaOH, $K = 0·0225$;
 In *N*/4 NaOH + *N*/4 NaCl, $K = 0·0234$;
 In *N*/4 NaOH + *N*/2 NaCl, $K = 0·0264$.

This accelerating influence of sodium chloride is difficult to explain,

but is analogous to its influence on the velocity of the catalytic hydrolysis of methyl acetate by hydroxides (compare Reicher, *Annalen*, 1885, 228, 257, and Arrhenius, *Zeit. physikal. Chem.*, 1887, 1, 110). It is, however, in marked contrast to a case studied by Koelichen (*Zeit. physikal. Chem.*, 1900, 33, 129), where the velocity of the condensation of acetone to diacetone alcohol in the presence of hydroxyl ions as catalyser is retarded by most neutral salts, including sodium chloride, but is accelerated by potassium sulphate.

The catalysing effect of various amino-bases on this transformation has been compared in $N/4$ aqueous solution. It is of interest to note that the comparison shows that the amines (with one or two exceptions) differ in their catalytic effect in much the same degree as their dissociation constants (compare Bredig, *Zeit. physikal. Chem.*, 1894, 13, 290), that is, in general in the fatty series the tertiary amines are weaker than the secondary amines containing the same alkyl radicles, but are about of the same strength as the corresponding primary amines.

The following table shows the relation between the velocity constants recorded in this paper and the dissociation constants of Bredig. The value for piperidine is put equal to 100 in each case :

	Velocity constant of the transformation.	Dissociation constant.
Methylamine	23.9	31.6
Dimethylamine	70.1	46.8
Trimethylamine	30.9	4.7
Ethylamine	20.2	34.9
Diethylamine	34.3	79.7
Triethylamine	13.3	40.5
Propylamine	22.0	29.7
<i>iso</i> Propylamine	14.6	33.5
<i>iso</i> Butylamine	14.2	19.6
<i>tert</i> -Butylamine	12.7	20.2
Allylamine	5.9	3.6
Piperidine.....	100.0	100.0

Here again the differences may be ascribed in all probability to the influence of the base on the ionisation of the active sodium salt, and the mechanism of the transformation may be further complicated in some cases by the formation of the less soluble salt of the organic base. The results, therefore, are not strictly comparable. This complication suggested further experiments in which an ester was used in place of the sodium salt, and it seemed of interest to investigate further the action of some secondary amines on the transformation, as it is well known that some of these, notably piperidine and diethylamine, have a marked catalytic effect on many organic reactions (especially condensations).

Preliminary experiments showed that the velocity of the transformation of the piperidine salt of the active Δ^2 -acid when dissolved in a

benzene solution of piperidine ($N/4$) was about sixteen times greater than that of the sodium salt dissolved in a corresponding aqueous solution of piperidine, and, further, that the piperidine salt itself was fairly rapidly transformed in benzene solution. In the subsequent experiments any disturbing influence of the carboxyl group was eliminated by conversion of the acid into the corresponding methyl ester. It was then found that the transformation of the ester of the Δ^2 -acid to that of the Δ^1 -acid proceeded in benzene (or chloroform) solution very much faster than the transformation of the sodium salt in aqueous solution under the catalytic influence of organic bases. It is probable that the transformation of the ester under these conditions is brought about by a different reaction. For in the first place the temperature quotients of the two reactions are widely different; thus the temperature quotient for fifteen degrees between 15° and 30° in the case of the ester with ($N/10$) piperidine as catalyser is 1.4, whilst in the case of the sodium salt with ($N/10$) sodium hydroxide as catalyser it is 6.2. Again, the effect of varying the concentration of the catalyser is different in the two cases; thus, comparing the effect of piperidine on the transformation of the ester in benzene with the effect of barium hydroxide on the transformation of the sodium salt in water, we found that the velocity constants in the first case were as 5 : 15 : 38 and in the second case were as 5 : 11 : 28, when the concentrations of the catalysers were as 1 : 2 : 4.

It is also interesting to note that the relative catalytic effect of mono-, di-, and tri-ethylamine in the two cases is quite different.

We have not investigated the effect of the medium on the velocity constants except in one case, where we found that the transformation proceeded ten times faster in benzene than in chloroform.

In Part I (*loc. cit.*), an attempt is made to explain the course of the transformation of the Δ^2 -acid to the Δ^1 -acid by assuming the addition of the elements of water and the subsequent elimination of water in a manner so as to leave the double linking in the Δ^1 -position. Similar explanations, which can be extended to instances of catalysis by a primary or secondary amine, are very frequently adopted in organic chemistry, but in the case of the ester, where some tertiary amines have an enormous catalytic effect on its transformation, such an explanation (even with the assumption of a temporary pentavalency of the nitrogen atom) is hardly possible.

EXPERIMENTAL.

The sodium salt of the d - $\Delta^{2 \text{ (or 3)}}$ -dihydro-1-naphthoic acid required for this work was prepared as described in Part I (*loc. cit.*). It was, however, discovered that, whilst the racemic acid was readily

soluble in cold petroleum (b. p. 60—70°), the dextro-acid was almost insoluble. It was therefore preferable to obtain the pure dextro-acid by the crystallisation from light petroleum of an acid separated from a partially purified *l*-menthylamine salt. The yield is much better than that obtained by the method given in Part I as the repeated crystallisation of the menthylamine salts is accompanied by great loss of material. In this way it is also easy to prepare the pure lævo-acid. A number of mother liquors from several preparations of the *l*-menthylamine salt of the dextro-acid was concentrated and allowed to stand at 0° for several days. From the oily mass a small crop of crystals separated. These had $[\alpha]_D$ in alcohol -90° (the pure [*l*+*l*] salt would have $[\alpha]_D$ about 130°). The acid obtained from this salt after two crystallisations from light petroleum yielded the pure lævo-isomeride in the form of beautiful, long, lustrous needles melting at 103° . The specific rotation was determined in chloroform :

0.3185 made up to 20 c.c. gave -6.77° in a 1-dm. tube ; whence $[\alpha]_D = -212.55^\circ$.

A mixture of equal parts of this acid and the dextro-isomeride was readily soluble in cold petroleum, whilst the crystals left after the solvent had evaporated melted at 89° . The sodium salts of both the active isomerides are far less soluble in anhydrous alcohol than that of the racemic acid, so that a further purification is effected in the last stage of the preparation of the material.

Methyl Ester.—The methyl ester was prepared by the action of methyl iodide on the silver salt. It is a mobile oil, boiling without decomposition at 160° under 12 mm. pressure. The preparation had a high positive rotation, but as it was prepared from a specimen of sodium salt which was not quite free from racemate, the actual value is not recorded here.

Determinations of the Velocity of the Transformation.—The velocity constants were calculated from the equation for unimolecular reactions, $K = 1/t \log c_0/c_t$, and were determined by polarimetric observations made in a jacketed tube round which circulated water coming from a reservoir of constant level and passing through a long copper coil immersed in a thermostat. For each determination about 0.27 to 0.3 gram of the sodium salt (or methyl ester) in 20 c.c. of the solvent was used, a concentration which gives an initial rotation of nearly 6° . The first few readings often gave erratic values, which were discarded. The polarimeter gave readings accurate to $\pm 0.01^\circ$, so that numerous values of the constants could be obtained.

Two examples of the results thus obtained are given, the remainder being tabulated below :

TABLE I.

In $N/4\text{Ba}(\text{OH})_2$ at 30° .

Time in hours.	Rotation.	K .
0.0	5.16°	—
2.0	4.41	0.0341
2.5	4.21	0.0354
3.0	4.02	0.0361
3.5	3.88	0.0354
4.0	3.71	0.0341
4.3	3.60	0.0360
4.7	3.52	0.0356
5.0	3.41	0.0360
5.3	3.29	0.0367
5.7	3.23	0.0359
6.2	3.09	0.0356
6.7	2.98	0.0358
8.6	2.48	0.0369
9.2	2.31	0.0375
9.8	2.24	0.0370
23.3	0.73	0.0365
∞	0.00	—

Mean $K = 0.0361$.

TABLE II.

In $N/4\text{C}_2\text{H}_5\cdot\text{NH}_2$ at 30° .

Time in hours.	Rotation.	K .
0.0	5.20°	—
6.0	4.96	0.00202
11.3	4.83	0.00209
22.3	4.57	0.00213
29.3	4.45	0.00202
35.0	4.32	0.00206
46.5	4.05	0.00215
53.0	3.92	0.00216
59.3	3.82	0.00212
71.3	3.62	0.00209
75.7	3.52	0.00213
83.0	3.44	0.00206
94.3	3.27	0.00205
101.0	3.18	0.00201
107.6	3.07	0.00206
118.7	2.90	0.00207
166.6	2.35	0.00202
∞	0.00	—

Mean $K = 0.00208$.

TABLE III.

Catalysis of Sodium Δ^2 (α^3)-Dihydronaphthoate.

Catalyser.	Concentration of catalyser.	Solvent.	Temp.	Velocity constant K .			
				No. of values.	Highest.	Lowest.	Mean.
NaOH	$N/2$	Water	30	16	0.0545	0.0514	0.0530
„	$N/4$	„	30	16	0.0236	0.0217	0.0225
„	$N/10$	„	30	14	0.00767	0.00723	0.00749
KOH	$N/2$	„	30	13	0.0557	0.0536	0.0550
„	$N/4$	„	30	22	0.0246	0.0231	0.0239
„	$N/5$	„	30	12	0.0184	0.0172	0.0179
„	$N/10$	„	30	16	0.00784	0.00743	0.00769
LiOH	$N/4$	„	30	20	0.0268	0.0244	0.0257
$\text{Ca}(\text{OH})_2$	$N/25$	„	30	21	0.00480	0.00455	0.00468
$\text{Sr}(\text{OH})_2$	$N/10$	„	30	11	0.0126	0.0118	0.0121
„	$N/10$	„	30	10	0.0124	0.0111	0.0118
„	$N/20$	„	30	19	0.00477	0.00454	0.00467
$\text{Ba}(\text{OH})_2$	$N/5$	„	30	18	0.0293	0.0264	0.0277
„	$N/10$	„	30	20	0.0118	0.0110	0.0113
„	$N/20$	„	30	6	0.00587	0.00502	0.00528
„	$N/25$	„	30	14	0.00374	0.00351	0.00364
Tetramethyl ammonium hydroxide	$N/4$	„	30	11	0.0187	0.0175	0.0181
Tetraethyl ammonium hydroxide	$N/4$	„	30	12	0.0208	0.0193	0.0201
Tetrapropyl ammonium hydroxide	$N/4$	„	30	11	0.0144	0.0134	0.0141
NaOH	$N/4$	25 % alcohol	30	8	0.0226	0.0212	0.0219
„	$N/4$	50 % „	30	13	0.0320	0.0299	0.0306
„	$N/4$	75 % „	30	20	0.0730	0.0674	0.0700
„	$N/2$	50 % „	30	17	0.0790	0.0757	0.0773

* With the levo-salt.

TABLE III (continued).
Catalysis of Sodium $\Delta^{2 \text{ (or 3)}}$ -Dihydronaphthoate.

Catalyser.	Concentration of catalyser.	Solvent.	Temp.	Velocity constant K .			
				No. of values.	Highest.	Lowest.	Mean.
NaOH	$N/4$	$N/2\text{NaCl}$	30°	9	0.0269	0.0252	0.0264
..	$N/4$	$N/4\text{NaCl}$	30	14	0.0242	0.0223	0.0233
..	$N/10$	$4N/10\text{NaCl}$	30	10	0.00942	0.00913	0.00926
..	$N/10$	Water	15	8	0.00138	0.00121	0.00129
Methylamine	$N/4$..	30	11	0.00256	0.00237	0.00247
Dimethylamine	$N/4$..	30	24	0.00745	0.00717	0.00723
Trimethylamine	$N/4$..	30	13	0.00334	0.00308	0.00319
Ethylamine	$N/4$..	30	16	0.00216	0.00201	0.00208
Diethylamine	$N/4$..	30	14	0.00368	0.00346	0.00355
Triethylamine	$N/4$..	30	13	0.00140	0.00127	0.00135
Propylamine	$N/4$..	30	15	0.00232	0.00219	0.00227
<i>iso</i> Propylamine	$N/4$..	30	14	0.00160	0.00146	0.00151
Allylamine	$N/4$..	30	18	0.00063	0.00058	0.00061
<i>n</i> -Butylamine	$N/4$..	30	13	0.00206	0.00190	0.00198
<i>is</i> Butylamine	$N/4$..	30	17	0.00156	0.00140	0.00147
<i>tert.</i> -Butylamine	$N/4$..	30	16	0.00137	0.00123	0.00131
Piperidine	$N/4$..	30	12	0.0108	0.0099	0.0103

Ammonia in $N/4$ aqueous solution has a very small catalytic effect, the velocity constant obtained being 0.00015. This value is, however, only approximate, as the solutions of the sodium salt in ammoniacal solution turn brown at the end of a fortnight. Aqueous pyridine ($N/4$) does not induce the transformation of the sodium salt, nor pyridine in benzene solution that of the methyl ester.

Catalysis of Methyl $\Delta^{2 \text{ (or 3)}}$ -Dihydro-1-naphthoate.—The experiments with the ester were carried out as with the sodium salt, except that in some cases the times were taken in minutes, owing to the speed of the transformation. In each such case the constants have been multiplied by sixty, to be comparable with the other constants. The amount of amine used in the formation of amide was very small during the time over which the observations extended.

TABLE IV.

Catalyser.	Concentration of catalyser.	Solvent.	Temp.	Percentage of ester converted to amide during the observations.	Velocity constant K .			
					No. of values.	Highest.	Lowest.	Mean.
<i>iso</i> Propylamine	$N/10$	Benzene	30°	7 % in 2 hours	10	0.193	0.167	0.179
..	$N/10$	Chloroform	30	26 % in 40 hours	8	0.0178	0.0156	0.0165
Triethylamine	$N/10$	Benzene dried with CaCl_2	30	—	11	0.786	0.741	0.754
..	$N/10$	Benzene dried with P_2O_5	30	—	11	0.798	0.750	0.778

TABLE IV (*continued*).

Catalyser.	Concentration of catalyser.	Solvent.	Temp.	Percentage of ester converted to amide during the observa- tions.	No. of values.	Velocity constant K .		
						Highest.	Lowest.	Mean.
Tripropylamine	N/10	Benzene	30°	—	15	0.144	0.121	0.135
<i>p</i> -Toluidine ...	N/10	„	30		Approximate mean K =			0.007
Piperidine	N/10	„	30	6 % in 13 mins.	16	1.202	3.138	3.831
„	N/10	„	15	7 % in 21 mins.	20	2.790	2.478	2.634
„	N/20	„	30	3 % in 42 mins.	22	1.596	1.398	1.496
„	N/40	„	30	1 % in 80 mins.	11	0.516	0.476	0.493
Ethylamine ...	N/10	„	30	7 % in 80 mins.	14	0.305	0.277	0.283
Diethylamine..	N/10	„	30	5 % in 80 mins.	17	0.777	0.716	0.749

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CXLVI.—*Estimation of Copper by Titanium Trichloride.*

By EZRA LOBB RHEAD.

FOR the quantitative estimation of copper, both gravimetric and volumetric methods are commonly employed. Of the former, the electrolytic process is that more generally adopted. It has the advantage of being applicable in the presence of iron and some other metals, thus necessitating less previous separation than most of the other gravimetric methods.

The solution, however, requires careful preparation and the adjustment of the current strength, size of cathode, strength of solution, temperature, and some other details demand special experience and skill in order to secure the best results. The precipitation is usually incomplete, and the last traces of copper have to be estimated colorimetrically. In works where many analyses are conducted at one time, much platinum is required, thus greatly increasing the prime cost.

Of the volumetric processes the iodide method is the one usually

admitted to be the best and is very generally adopted, although in some laboratories the cyanide process still survives. The difficulty of obtaining accurate results with the latter is, however, well known.

The iodide method is an excellent way of estimating copper under well-known and sharply-defined conditions, and yields good results. In addition to the care required in the preparation of the copper solution, the preparation of the starch solution and the amount added influence the result and the ease with which the end reaction is obtained. The necessity of maintaining the solution cold throughout the titration is sometimes overlooked, and there may be a loss of iodine and consequent reduction in the amount of copper found.

The determination of the end reaction also requires much practice, and the probabilities of the return of the blue colour after being discharged by thiosulphate cannot be calculated, nor can it in many cases be prevented.

Quite recently, Gerlinger (*Zeit. angew. Chem.*, 1906, **19**, 520) has called attention to these difficulties, which he ascribes to the precipitated cuprous iodide. He recommends the addition of a sufficient amount of potassium iodide to dissolve the precipitate, but the amount of iodide required for the purpose is in all cases very great, and in dilute solutions exceedingly so. In some estimations made by the author one gram of copper sulphate was dissolved in 200 c.c. of water, and portions of 5 c.c. = 0.025 gram taken. These were titrated with a solution of potassium iodide containing 100 grams per litre. Three determinations of the amount required to obtain a perfectly clear solution gave 73.5 c.c., 73.8 c.c., and 74 c.c. respectively; equal to 1158 times the weight of copper in the solution. In stronger solutions less is required.

The method of estimating copper described in this paper is free from these drawbacks and is equally accurate. It consists in reducing an acid solution of a cupric salt to which potassium thiocyanate has been added by means of titanium trichloride, a powerful reducing agent introduced by Knecht in 1903 (*Ber.*, **36**, 166, 1549). The behaviour of the solution is somewhat peculiar. Cupric thiocyanate is formed, but remains in solution, forming a brownish-coloured liquid.

On adding pure titanium trichloride to the solution this colour is discharged, cuprous thiocyanate being precipitated, and a colourless, or nearly colourless, solution remains. The end reaction is reached too gradually to be easily distinguished. If, however, a ferric salt be added to the solution, a deep red coloration is produced with the excess of thiocyanate and persists until the whole of the copper salt has been reduced to the cuprous state and precipitated. The red coloration is ultimately discharged by excess of titanium trichloride, showing that under the conditions of the experiment the copper was first affected.

Experiment showed that ferrous salts reduce cupric salts to the cuprous state very readily in acid solutions, and the amount of the reagent consumed was the same with or without the addition of ferrous compounds; the quantity of titanium trichloride required to reduce the ferric salt resulting from the oxidation of the ferrous by the cupric salt is identical with that required to reduce the corresponding quantity of the latter.

The determination of the end of the reaction was thus rendered very easy, the red colour of iron thiocyanate being so pronounced. The end reaction is as sharp as in titrations with permanganate, a single drop of a weak solution being sufficient to determine it.

The addition of the ferrous iron may be made to the solution of copper or to the standard titanium trichloride solution. In the latter case, the addition of the reagent causes an increase in the depth of colour in the copper solution until near the end, owing to the increase in the amount of iron added with the reagent. This method of adding iron is somewhat less convenient, but ensures the whole of it being present in the ferrous state, since it is mixed with the reducing agent. It interferes, however, with the cross standardisation by means of iron, since ferrous salts reduce cupric salts. If, however, the solution be standardised with pure copper, no difficulty is encountered, and the use of two solutions is avoided.

There is also an objection to adding iron to the reagent in estimating small quantities of copper and in very dilute solutions, as so little iron may be added as to render the end reaction indistinct.

It is, therefore, better in most cases to use pure titanium trichloride and add a ferrous salt to the copper solution. At present the commercial titanium salt contains iron, and the original experiments were made with this product. In view of the fact that cross standardisation was thus rendered impossible, Messrs. Peter Spence and Sons, Ltd., of Manchester, very kindly prepared and supplied me with some of the pure salt free from iron, so as to place the accuracy of the method beyond doubt.

In carrying out the titration, the usual necessary precautions in the use of the reagent must be observed, and the analyses must be made in cold solution. The solution must be preserved from the air unless check determinations are done with every batch of estimations. Even this is less satisfactory than using a suitable apparatus, with a hydrogen generator attached (compare Knecht, *J. Soc. Dyers*, 1903, 19, 169, also Sutton's *Volumetric Analysis*, 9th ed., 224). The special arrangement is, when once set up, more simple to use than an ordinary burette.

Solutions of titanium trichloride of various strengths were used. The usual solution was made by boiling 50 c.c. of the strong solution

(commercial 20 per cent.) with 50 c.c. of strong hydrochloric acid and diluting to two litres. Its strength corresponded approximately to 0.003 gram of copper per c.c.

The results obtained were as follows:

Standardisation by Iron.—Seven grams of ferrous ammonium sulphate were dissolved in water and made up to a litre (1 c.c. = 0.001 gram Fe). The solution was oxidised with potassium permanganate run in from a burette.

(1) 50 c.c. iron solution required 19.4 c.c. titanium trichloride.

(2) „ „ „ „ 19.4 „ „ „

(3) „ „ „ „ 19.35 „ „ „

Mean..... 19.38

$$\text{Fe equivalent} = \frac{0.05}{19.38} = 0.00258 \text{ gram.}$$

Copper Solution.—Recrystallised copper sulphate equal to 0.99765 gram of copper was weighed out and made up to a litre.

Potassium Thiocyanate Solution.—One hundred grams of the salt were dissolved and made up to a litre. From 10 to 20 c.c. were added to each titration.

(1) 50 c.c. copper solution required 17.00 c.c. titanium trichloride.

(2) „ „ „ „ 17.05 „ „ „

(3) „ „ „ „ 17.00 „ „ „

Fe value of solution = 0.00258.

$$\text{Cu value} = 0.00258 \times \frac{63.5}{56} = 0.00293.$$

Copper found = $0.00293 \times 17.02 = 0.04986$ gram, equal to 99.95 per cent. of the copper present in the pure salt.

The amounts of potassium thiocyanate, acid (either sulphuric or hydrochloric), and water used were varied in a large number of experiments, but no alteration in the quantity of titanium trichloride could be detected.

Titration in Presence of Ferric and Cupric Salt.

Copper solution.	Iron alum solution.	H ₂ SO ₄ (1 : 1).	TiCl ₃ solution.*
20 c.c.	—	10 c.c.	10.5 c.c.
—	20 c.c.	10 „	12.05 „
20 „	20 „	10 „	22.5 „
20 „	20 „	10 „	22.5 „

* This was a weaker solution than that used in the foregoing experiments.

Total copper and iron may therefore be estimated in the same solution.

The presence of such salts as ammonium chloride, sodium acetate, zinc sulphate or chloride, ferrous sulphate, and stannic chloride exerts no influence on the course of the reaction.

Effect of Temperature.—At 80° the reagent is decomposed with precipitation of titanium dioxide. At 40° the first addition of a few c.c. discharged the red colour, but it quickly returned as the liquid cooled. Further additions were made and the amount finally required was the same as when cold, making a slight allowance for the oxidation resulting from longer exposure during titration.

TiCl ₃ required in the cold	10.65 c.c.
„ „ at 40° and cooling down	10.72 „

Below 30° the amount required was not affected by variation in temperature.

Effect of Nitric Acid.—Owing to its reduction by titanium trichloride, this acid must be absent.

Ferric Salts.—Iron in the ferric state must be absent from the solution titrated, or the copper value of the amount of iron so present deducted from the result after it has been separately determined. The iron may be removed as acetate in the ordinary manner before titrating the copper.

To test the method by comparison with others, a sample of copper was analysed by the iodide, electrolytic, and the method here described, with the following results :

Method.	Copper taken.	Copper found.	Percentage.
Electrolytic	0.25 gram	0.2498 gram	99.92
Titanium trichloride	0.25 „	0.2497 „	99.88
Iodide	0.25 „	0.2496 „	99.84

In conclusion, I must gratefully acknowledge the kindness of Dr. Knecht and of Messrs. Spence and Sons, Ltd., for providing me with the titanium salt.

My thanks are also due to Mr. G. H. Gray and Miss Eva Hibbert, who have assisted me with the analytical work.

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CXLVII.—*The Gum of Cochlospermum Gossypium.*

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A SMALL deciduous tree, *Cochlospermum Gossypium*, belonging to the *Bixineae*, which grows abundantly in the forests of the North-West Himalaya, and extends across the central table-land of India, furnishes a gum, which occurs in irregular, rounded, translucent lumps of a pale buff colour. This gum resembles tragacanth in absorbing a large quantity of water and swelling up to many times its original size; it is sold in the Indian bazaars as a substitute for tragacanth. Several pounds of the gum were received at the Imperial Institute from the Indian Government.

It is remarkable among the gums for its property of slowly giving off acetic acid when exposed to moist air; if a bottle of it is opened a distinct odour of acetic acid is noticed. This property is also possessed by the gum of *Sterculia urens*, and is mentioned by Guibourt (*Pharm. J.*, 1855, 15, 57).

The gum does not dissolve to any extent in water. One gram of the powdered substance was mixed with 100 c.c. of water and shaken from time to time during three days; the supernatant liquid was filtered, and a portion of it, on evaporation, gave a residue the weight of which showed that the 100 c.c. had dissolved 8.4 per cent. of the gum taken; this most probably was not all in true solution, but included minute particles of jelly which had passed through the pores of the filter-paper.

The gum does not give any blue coloration with solution of iodine, and, consequently, is free from starch.

Lemeland (*J. Pharm. Chim.*, 1904, 20, 253) determined the amount of furfural and mucic acid yielded by the gum, and concluded that 100 grams of the dry substance should yield on hydrolysis 33.0 grams of pentoses and 15.3 grams of galactose; he also succeeded in isolating galactose.

In carrying out this work the lines of O'Sullivan's researches (*Trans.*, 1884, 45, 41; 1891, 59, 1029; 1901, 79, 1164) have been followed. This author has shown that gums are not carbohydrates, with which they are often erroneously classed, but are acids of high molecular weight, from which, by hydrolysis, various sugars can be separated, leaving a more stable acid of lower molecular weight, which still possesses gum-like properties. He further showed that by gentle hydrolysis evidence can be obtained of the existence of a number of intermediate acids lying between the natural gum and this compara-

tively stable acid. The latter thus serves as a nucleus with which the residues of various sugar molecules are combined to form the gum.

From the substance under investigation a stable acid was obtained having a composition corresponding to the formula $C_{23}H_{36}O_{21}$, for which the name *gondic acid* is proposed, from "gond," the Hindustani for gum. It differs by one molecule of water from the arabic acid or λ -arabinosic acid and the geddic acid described by O'Sullivan, each of which has the formula $C_{23}H_{38}O_{22}$, and by one carbon atom from the tragacanth-xylan-bassoric acids, $C_{24}H_{36}O_{21}$, of the same author. Like some of the gum acids, when it unites with bases, it forms salts by addition without any elimination of water. It is probably a dibasic acid at least, since a monobasic acid of the same composition and neutralising power would only contain eleven or twelve carbon atoms in its molecule, and an acid of such low molecular weight would be less likely to possess the properties of a gum.

Xylose and a hexose were found in the liquids obtained on hydrolysing the gum and removing the gondic acid.

As regards the gum itself, it was found to yield 14 per cent. of acetic acid, equivalent to 18 per cent. when calculated on the dry and ash-free substance; it thus proves to be an acetyl derivative of a gummy substance. By the action of sodium hydroxide solution in the cold, the acetyl group was removed and a gummy substance was obtained which had acid properties. To this the name of *α -cochlosperminic acid* may be given.

Analyses were made both of the gum and of the *α -cochlosperminic acid*. From these data the following explanation of the constitution of the gum suggests itself: *α -cochlosperminic acid* may be a *hexosan-xylosan-gondic acid*, $C_6H_{10}O_5$, $C_5H_8O_4$, $C_{23}H_{36}O_{21}$, or $C_{24}H_{54}O_{20}$, and the gum itself a tetra-acetyl derivative of this substance, some acetic acid having been slowly lost during keeping, thus reducing the yield of acetic acid. This view, however, appears almost too simple, and a more elaborate system of examination may prove the composition to be more complex. Moreover, the neutralising power found for *α -cochlosperminic acid* is too high to be consistent with this view, unless it was due to some impurity.

EXPERIMENTAL.

On breaking up the gum into small fragments (it is of a very tough nature) and then picking out those which are not discoloured, a pure, white sample can be obtained. Such a sample, after further powdering, was found to lose, when dried at 100° , 15.5 per cent. of its weight, and to contain 5.2 per cent. of ash, equivalent to 6.2 per cent. in the dry gum. When the dried powder (preparation *P*) was exposed to air,

it reabsorbed very nearly the same weight of water which it lost at 100°.

In order to remove ash constituents, 6 grams of selected gum were allowed to stand in contact with a mixture of 11 c.c. of strong hydrochloric acid solution and 33 c.c. of absolute alcohol; the proportion of water present was sufficient to cause the gum to swell. After twenty minutes, 32 c.c. of absolute alcohol were added; this caused signs of desiccation of the gum; after an hour or two the alcohol was poured off and fresh alcohol was added and left in contact for some hours, and then was decanted; this washing was repeated about twenty times. The purified substance (preparation *Q*) was then dried over calcium chloride in a vacuum; the desiccating action of the alcohol had rendered it far less tough and it was easily reduced to powder. It now contained, when dried at 100°, 1.1 per cent. of ash.

Another specimen of selected gum was freed from ash in a slightly different way; it was left in contact with a mixture of equal volumes of strong hydrochloric acid solution and water for twenty minutes, and was then treated repeatedly with 75 per cent. alcohol, which was weak enough to allow it to remain in gelatinous lumps and not to desiccate it. The lumps were dried at 100° and powdered. This preparation (*R*) when dried at 100° lost 8.4 per cent. of its weight; after being dried at this temperature it contained only 0.25 per cent. of ash.

In the following analyses of these three preparations the percentages are calculated on the dry and ash-free gum.

Preparation *P*.

0.3094 gave 0.4730 CO₂ and 0.1552 H₂O. C = 44.45; H = 5.94.

Preparation *Q*.

0.3408 gave 0.5599 CO₂ and 0.1799 H₂O. C = 45.31; H = 5.93.

0.3723 „ 0.6099 CO₂ „ 0.1918 H₂O. C = 45.18; H = 5.78.

Preparation *R*.

0.2657 gave 0.4366 CO₂ and 0.1424 H₂O. C = 44.92; H = 5.97.

0.2864 „ 0.4723 CO₂ „ 0.1513 H₂O. C = 45.09; H = 5.89.

C₃₄H₅₁O₂₇(OAc)₃ requires C = 44.94; H = 5.62 per cent.

C₃₄H₅₀O₂₆(OAc)₄ „ C = 45.41; H = 5.59 per cent.

Yield of Acetic Acid.

Twenty-two grams of the gum were heated with 200 c.c. of a solution containing 13 grams of sulphuric acid on a water-bath for two hours and then distilled with a naked flame for twenty minutes. The distillate was treated with barium carbonate, filtered, mixed with

phosphoric acid, and distilled. To the distillate, silver oxide was added, and from the solution crystals were obtained which proved to be silver acetate, for, on ignition :

0.2814 gave 0.1817 Ag. $\text{Ag} = 64.57$.

$\text{C}_2\text{H}_3\text{O}_2\text{Ag}$ requires $\text{Ag} = 64.67$ per cent.

The liquid remaining in the distilling flask after the first distillation was treated with barium carbonate to remove sulphuric acid and was then distilled with phosphoric acid ; the distillate was redistilled and treated with silver oxide and crystals of silver acetate were again obtained.

0.2485 gave 0.1600 Ag. $\text{Ag} = 64.39$ per cent.

There is thus no doubt that acetic acid is one of the products of hydrolysis.

Two hundred and thirty-two grams of the gum were hydrolysed by heating with 3 per cent. sulphuric acid for thirteen hours on a water-bath. A portion of the resulting liquid, representing 17 grams of the gum, was distilled in a current of steam and the amount of acid in the distillate was determined by means of a standard solution of sodium hydroxide, using phenolphthalein as the indicator. An amount of acetic acid was found equivalent to 14.4 per cent. of the gum, or 18.2 per cent. of the dry ash-free substance, allowing for the presence of 16 per cent. of water and 5 per cent. of ash.

In two experiments, some of the powdered gum was divided and examined as follows : a portion weighing 1.1594 grams was warmed for eight hours in a water-bath with 40 c.c. of $N/4$ sodium hydroxide solution ; the mixture was then acidified with 6 c.c. of phosphoric acid of sp. gr. 1.5 and distilled, using a bath of calcium chloride solution ; water was added and three more distillates were obtained. Using sodium hydroxide solution and phenolphthalein as an indicator, it was found that the yield of acetic acid was 13.1 per cent. or, allowing for 18 per cent. of water, 16.0 per cent. of the dry gum.

The second portion, which weighed 1.3113 grams, was dried at 100° in a water-oven and lost 0.2363 gram, equivalent to 18.0 per cent. The dry residue was then treated in the same manner as the first portion and it was found that the yield of acetic acid was 13.7 per cent. of the gum or 16.7 per cent. of the dry gum or 17.8 per cent. of the dry and ash-free gum.

These experiments show that no acetic acid is lost by the gum in the course of drying at 100° in a water-oven.

Preparation of α -Cochlosperminic Acid.

A portion of the gum weighing 100 grams was left in contact with 2 litres of 5 per cent. sodium hydroxide solution. In the course of a few days it swelled so as to occupy apparently the whole two litres of liquid, but the swelling caused little or no increase in the total volume. The mixture was left at the ordinary temperature for a considerable time; a portion was then removed and neutralised with standard acid and it was found that part of the sodium hydroxide had been neutralised, and that 100 parts of dry gum were equivalent to roughly 20 parts of acetic acid in neutralising effect. It thus appeared probable that the acetyl groups had been removed by the sodium hydroxide.

After various trials the following method was found to be the best for the preparation of α -cochlosperminic acid. A portion of the above liquid, which was a thick mucilage, was mixed with an equal volume of normal hydrochloric acid solution, which nearly neutralised the sodium hydroxide; after standing for a few days it became much less viscous. It was then mixed with one-tenth of its volume of strong hydrochloric acid solution. It was now moderately clear. In order to remove impurities it was filtered, placed in tubes of parchment paper, and dialysed until all the hydrochloric acid was removed; a bright clear solution was thus obtained.

The solution yielded by dialysis does not give a precipitate when mixed with alcohol alone, but when an acid or a salt in solution is added to the mixture with alcohol, a white, gummy substance separates, a property characteristic of colloids.

The solution contained 0.611 gram of dry matter in 100 c.c., of which 0.060 gram was ash; a column of it 200 mm. in length was found to possess a rotatory power of $\alpha_D + 0^\circ 38'$, whence $[\alpha]_D + 57^\circ$ for dry and ash-free α -cochlosperminic acid.

Some solution similarly prepared was mixed with nearly twice its volume of 97 per cent. alcohol and one-fiftieth of its volume of strong hydrochloric acid solution; the precipitate produced was separated, washed with alcohol, and dried over calcium chloride in a desiccator. Prepared in this way (*M*), the acid was a white, granular, amorphous substance containing only 0.24 per cent. of ash.

A second preparation (*N*) of the acid was made in a very similar manner, but sulphuric acid was used to neutralise the sodium hydroxide before dialysing and some hydrochloric acid was used later. This preparation contained 0.8 per cent. of ash. After drying at 100° , the following numbers were obtained on analysis:

Preparation M.

0.2115 gave 0.3315 CO_2 and 0.1115 H_2O . $\text{C} = 42.85$; $\text{H} = 5.87$.

0.2137 „ 0.3320 CO_2 „ 0.1088 H_2O . $\text{C} = 42.47$; $\text{H} = 5.67$.

Preparation N.

0.2119 gave 0.3346 CO_2 and 0.1090 H_2O . $\text{C} = 43.41$; $\text{H} = 5.76$.

0.1728 „ 0.2697 CO_2 „ 0.0895 H_2O . $\text{C} = 42.79$; $\text{H} = 5.79$.

$\text{C}_{34}\text{H}_{54}\text{O}_{30}$ requires $\text{C} = 43.31$; $\text{H} = 5.73$ per cent.

The percentages are calculated on the dry and ash-free substance.

The dialysed solution was an almost colourless, gummy liquid, and on evaporation left the α -cochlosperminic acid in transparent, gum-like flakes, which were insoluble in water. The white form obtained by precipitating with alcohol is brittle and easily powdered; with water it gelatinises, but does not dissolve. That the substance was really de-acetylated was proved by distilling a portion of it with sulphuric acid, when the distillate contained no acetic acid.

The substance has acid properties and an attempt was made to determine its neutralising power by grinding some of the preparation *M*, and dividing the powder into two weighed portions. In one portion the loss at 100° was determined; the other was treated with $N/10$ sodium hydroxide solution in a closed flask. After about half an hour it had all dissolved, and the liquid had acquired a pale yellow tint; two days later the excess of sodium hydroxide was determined, and the neutralising power of the dry substance was found to be equivalent to a "barium oxide value" of 20.2.* This result was much higher than was expected considering the barium oxide value of the soluble gonic acid.

The Gum Acids.

In order to ascertain the composition of the gum it was decided to hydrolyse it by means of sulphuric acid, and then to separate and examine the products obtained. Several such hydrolyses were made, and it was found that the gum when thus treated yielded sugars and one or more gum acids.

The gum when warmed for about fourteen hours with $2\frac{1}{2}$ or 3 per cent. sulphuric acid solution slowly dissolved, and the resulting liquid when mixed with alcohol yielded a precipitate of the gum acid as a soft, dough-like mass. In some experiments alcohol was added at once to the liquid, in others the sulphuric acid was previously removed by the addition of barium carbonate, the gum acid being simultaneously converted into a soluble barium salt. The precipitate was purified by repeatedly dissolving it in water and reprecipitating

* The weight of barium oxide required to neutralise 100 parts of the dry acid.

with alcohol, the final purification being effected by acidifying the aqueous solution with hydrochloric acid and submitting it to dialysis in a tube of parchment paper. When necessary, the liquids were decolorised by percolation through animal charcoal. The gum acid passed through the parchment paper very slowly, and consequently a large proportion of it was left in the paper tube free from inorganic constituents. It was precipitated by the addition of alcohol, and dried by leaving it over calcium chloride in a desiccator.

Obtained in this way, it is a white, granular substance, easily reduced to powder. It remains unaltered on exposure to air and does not deliquesce, but if left moist with alcohol on a filter paper the alcohol absorbs the atmospheric moisture, and this is transferred to the acid, rendering it gummy and stopping all further filtration. In consequence of this, filtrations of the alcoholic precipitates must be performed over calcium chloride under a large glass shade to ensure a dry atmosphere. The substance has a pleasant acid taste and dissolves readily in water, and the aqueous solution when evaporated leaves transparent, gum-like scales, which, unlike the scales obtained by evaporating the solution of the de-acetylated gum, are still soluble in water. On heating, it chars without melting.

The first preparation (*A*) made was examined before it had been submitted to dialysis. After drying at 100° , it contained 5.7 per cent. of ash.

0.1969 gave 0.2891 CO_2 and 0.0916 H_2O . $\text{C} = 42.46$; $\text{H} = 5.48$.

0.2015 „ 0.2967 CO_2 „ 0.0959 H_2O . $\text{C} = 42.59$; $\text{H} = 5.61$.

$\text{C}_{23}\text{H}_{36}\text{O}_{21}$ requires $\text{C} = 42.59$; $\text{H} = 5.56$ per cent.

The percentages are calculated on the dry and ash-free substance.

The dialysis method of purification was then applied to this same product (*A*). After dialysis the rotatory power of the substance in solution was found to be $[\alpha]_D + 93^{\circ}$.

The acid was then separated by precipitation and the product (*B*), which was almost free from ash, after drying at 100° yielded the following results :

0.2175 gave 0.3366 CO_2 and 0.1082 H_2O . $\text{C} = 42.21$; $\text{H} = 5.53$.

0.2123 „ 0.3293 CO_2 „ 0.1049 H_2O . $\text{C} = 42.30$; $\text{H} = 5.49$.

These results agree with those obtained before dialysis. The neutralising power was then determined in terms of the amount of barium oxide required to neutralise 100 parts of the acid dried at 100° , using a standard solution of barium hydroxide with phenolphthalein as the indicator. This barium oxide value was found to be 24.5. $\text{C}_{23}\text{H}_{36}\text{O}_{21}$ requires a barium oxide value of 23.6.

Another preparation was made from 80 grams of the gum, using

barium carbonate to remove the sulphuric acid and convert the gum acids into their barium salts. The barium salts were precipitated by alcohol, and when water was added to the precipitate the resulting liquid separated into two layers, resembling the separation of phenol when mixed with water. The two layers were treated separately. The lower layer yielded 6 grams of an acid (preparation *C*) which had a barium oxide value of 20.8; it contained, however, about 0.4 per cent. of ash. The upper layer yielded 4 grams of an acid (preparation *D*) which had a barium oxide value of 23.9, uncorrected for ash.

The effect of fractional precipitation was next tried with these two preparations; the acids were dissolved in water and alcohol was added to the solutions in quantities insufficient to cause complete precipitation. The precipitates obtained were further purified by redissolving and reprecipitating, except in the case of the third fraction of *D*, which was too small to be reprecipitated. The barium oxide values of the three fractions of *C* were found to be 18.0, 18.4, and 17.4, and those of the three fractions of *D* were 20.9, 20.8, and 23.4. *C* and *D* were thus mixtures containing acids with more sugar residue in the molecule than gondic acid and lying between that acid and the gum. A hexosan-pentosan-gondic acid would have a barium oxide value of 16.2 and a pentosan-gondic acid would have one of 19.6. The amounts of *C* and *D* available were insufficient to permit of a complete investigation of the intermediate acids, and the values given are not corrected for ash.

In order to obtain a further quantity of the acid, another hydrolysis was made, employing 500 grams of the gum, and from this two preparations, *E* weighing 36 grams and *F* weighing 12 grams, were obtained. They were prepared by using barium carbonate as a neutralising agent, and were purified by dialysis. Preparation *E* was not quite free from barium oxide; the amount of this was ascertained and allowed for in the determinations. It had a barium oxide value of 24.7, and its rotatory power was $[\alpha]_D + 91^\circ$.

Preparation *F* had a barium oxide value of 24.4 and its rotatory power was $[\alpha]_D + 93^\circ$.

Experiments were made with the object of separating this acid into smaller molecules by further hydrolysis, but it appeared to be resistant except to powerful action, when a general decomposition occurred. Some of preparation *E* was warmed in a water-bath for half an hour with one-tenth of its weight of sulphuric acid and twenty times its weight of water; the gum acid was separated and its barium oxide value was found to be 25.0. Another portion of preparation *E* was warmed in a water-bath for one hour with half its weight of sulphuric acid and twenty times its weight of water; the gum acid was separated and its barium oxide value was found to be 26.7. Hydrolysis with still

stronger sulphuric acid solution was then tried, employing 9 grams of preparation *E*, and warming it in a water-bath for eight hours with three times its weight of sulphuric acid and thirty times its weight of water; it was found to have undergone much decomposition, but the products could not be satisfactorily isolated.

These results seem to point to the existence of a gum acid of considerable stability, having a barium oxide value of about 24 and a rotatory power of about $[\alpha]_D + 93^\circ$. Twenty grams of the preparation *E* were then separated by fractional precipitation with alcohol into three fractions, each of which was redissolved and reprecipitated by alcohol; the three products *Ea*, *Eb*, and *Ec* were found to have barium oxide values of 23.7, 23.7, and 24.1 respectively, allowance having been made for the small quantities of barium oxide they contained derived from the barium oxide in preparation *E*. The first of these products was dissolved and precipitated by alcohol in the presence of a little sulphuric acid, again dissolved, and precipitated by alcohol. The precipitate *Eaa* was found to have a barium oxide value of 23.7 and a rotatory power of $[\alpha]_D 97.7^\circ$; portions of it, after drying at 100° , yielded the following results:

0.2142 gave 0.3343 CO_2 and 0.1089 H_2O . C = 42.66; H = 5.66.

0.1918 „ 0.2995 CO_2 and 0.0969 H_2O . C = 42.70; H = 5.63.

$\text{C}_{23}\text{H}_{36}\text{O}_{21}$ requires C = 42.59; H = 5.56 per cent.

The ash in each case was 0.0005 gram and the percentages are calculated on the dry and ash-free substance.

O'Sullivan (Trans., 1891, 59, 1075) found that the gum acids when dry are anhydrides, and form addition compounds with barium oxide without elimination of water. In order to determine whether this is the case with gonic acid, the barium salt was prepared from a portion of *Eaa* by neutralising it with barium hydroxide solution, using phenolphthalein as the indicator, and then precipitating with alcohol. A portion of this salt, after drying at 100° , gave the following numbers: 0.2927 gave 0.3508 CO_2 , 0.1187 H_2O , and 0.073 BaCO_3 . C = 34.20; H = 4.51.

$\text{C}_{23}\text{H}_{36}\text{O}_{21} \cdot \text{BaO}$ requires C = 34.46; H = 4.49 per cent.

$\text{C}_{23}\text{H}_{34}\text{O}_{20} \cdot \text{BaO}$ „ C = 35.25; H = 4.34 per cent.

This result proves that gonic acid resembles the other acids in being an anhydride, and forming salts by addition, not by replacement. This conclusion is independent of any particular formula, since 100 parts of an acid containing 42.7 per cent. of carbon uniting with 23.7 parts of barium oxide give a salt containing 34.52 per cent. of carbon if an addition product is formed, but if 2.8 parts of water (the equivalent of 23.7 of barium oxide) are eliminated, the resulting salt contains 35.32 per cent. of carbon.

It was noticed that, like the arabinic acid prepared by Neubauer (*J. pr. Chem.*, 1854, **62**, 193) from gum arabic, gondic acid is rendered less easily soluble in water by prolonged drying at 100°. It was also found that by treatment with nitric acid of sp. gr. 1.50 gondic acid yields a nitrated derivative which is precipitated by the addition of water and is soluble in alcohol.

The Sugars.

From the liquids from which the gum acids had been precipitated by means of alcohol, two sugars were isolated, although with considerable difficulty.

The first appeared to be a hexose and crystallised in rosettes of lancet-shaped crystals. It had a sweet taste and a melting point of about 135°. When dried at 100° its rotatory power was $[\alpha]_D + 58^\circ$ and on analysis :

0.2024 gave 0.3005 CO₂ and 0.1224 H₂O. C = 40.49 ; H = 6.72.

C_nH_{2n}O_n requires C = 40.00 ; H = 6.67 per cent.

It yielded a yellow osazone melting at 157—159° and completely at about 160°, sparingly soluble in hot water, but much more soluble than dextrosazone. Whether this sugar is galactose not quite free from impurities, or whether it is a new sugar, could not be determined with certainty owing to the small quantity obtained, but it differed from galactose in the appearance of its crystals.

The second sugar possessed a rotatory power of $[\alpha]_D + 24^\circ$, and is doubtless xylose.

In conclusion, I desire to express my best thanks to Professor Wyndham R. Dunstan for suggesting this work, and for the valuable advice he has given me in carrying it out.

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CXLVIII.—*Steric Hindrance in the Naphthalene Series.*

By CLARENCE SMITH.

THE facility with which 1:8-naphthalene derivatives form ring compounds is usually considered to indicate that substituents in the peri-position are relatively situated very similarly to those in the ortho-position in a benzene or naphthalene nucleus. If this be so, the phenomenon of steric hindrance should be exhibited by certain naphthalene compounds having substituents in positions 1, 2, and 8,

and this explanation has been advanced to account for the peculiar behaviour of certain 2:8-derivatives, although exact experimental data are wanting.

Some years ago Witt (*Ber.*, 1888, 21, 3483) found that β -naphthylamine-8-sulphonic acid reacted with diazotised sulphanilic acid to form a diazoamine. Similar results have been obtained with diazonium salts of less molecular weight; it is worthy of mention, however, that in the production of these yellow diazoamines the red colour of the solution is the more pronounced the lower the molecular weight of the diazonium salt used, a result which points to the possibility of a small quantity of the aminoazo-compound being formed, although attempts to isolate such substances from the mother liquors were unsuccessful, as also were experiments undertaken with a view to the conversion of the diazoamino- into the aminoazo-compound. Evidently, with a substituent of large molecular volume in position 8 the intramolecular change is rendered impossible, or is very largely hindered, so that the diazo-complex cannot enter position 1 to form an aminoazo-compound. In accordance with this deduction, it was found that dimethyl- β -naphthylamine-8-sulphonic acid does not react with diazonium salts.

The molecular volume of the nitro-group is much less than that of the sulphonic acid group, and consequently 8-nitro- β -naphthylamine yields aminoazo-compounds in the usual way, although the effect of steric hindrance is manifested by the inability of such compounds to form acetyl derivatives.

The well-known difficulty of obtaining dyes from "G" salt in dilute solution is also due to steric hindrance, the effect of which has been illustrated by comparing the rates at which "G" and "R" salts respectively unite with diazonium compounds under identical conditions.

Hewitt and Mitchell have recently published the results of experiments on the mobility of the halogen atom in 1-bromo- β -naphthol, in which they have shown that the bromine atom is almost instantaneously displaced by diazo-complexes in alkaline solution. Owing to steric hindrance, 1-bromo- β -naphthol-8-sulphonic acid does not react with diazonium salts, whereas the halogen in 1-bromo- β -naphthol-6-sulphonic acid is displaced as readily as from 1-bromo- β -naphthol itself.

EXPERIMENTAL.

Sodium p-Toluenediazo- β -aminonaphthalene-8-sulphonate,
 $C_7H_7N_2 \cdot NH \cdot C_{10}H_6 \cdot SO_3Na.$

To a solution containing 8.16 grams of sodium β -naphthylamine-8-sulphonate and excess of sodium acetate in 500 c.c. of water was

slowly added the solution of the diazonium chloride prepared from 3.6 grams of *p*-toluidine. The mixed solutions immediately became dark red; excess of solid sodium acetate was added, and the orange-red precipitate was collected after fifteen hours, well washed with hot water, dried, and crystallised from alcohol. The diazoamine separates from this solvent in yellowish-brown needles, which darken at 215° and melt and decompose at 219°.

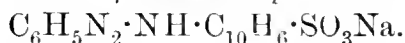
0.7000 gave 0.1306 Na_2SO_4 . $\text{Na} = 6.04$.

0.1002 „ 9.9 c.c. moist nitrogen at 18.5° and 772.5 mm. $\text{N} = 11.7$.

$\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_3\text{SNa}$ requires $\text{Na} = 6.3$ and $\text{N} = 11.6$ per cent.

The substance does not develop a characteristic coloration with concentrated sulphuric acid, and is decomposed by cold concentrated hydrochloric acid, the products of fission yielding a red precipitate with an alkaline solution of β -naphthol.

Sodium Benzenediazo- β -aminonaphthalene-8-sulphonate,

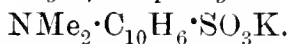


This substance is precipitated when equivalent quantities of sodium β -naphthylamine-8-sulphonate and benzenediazonium chloride react in the presence of excess of sodium acetate. From the dark red solution a reddish-brown precipitate separated, which was collected, washed, dried, and rapidly crystallised from hot water. Light yellow crystals were obtained which were sparingly soluble in alcohol, and insoluble in other organic solvents.

0.1332 gave 14.4 c.c. moist nitrogen at 23° and 781 mm. $\text{N} = 12.2$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_3\text{SNa}$ requires $\text{N} = 12.0$ per cent.

Potassium Dimethyl- β -naphthylamine-8-sulphonate,



Twenty grams of sodium β -naphthylamine-8-sulphonate and 12 grams of sodium hydroxide were dissolved in 125 c.c. of water and the solution warmed to 50–60° on the water-bath. An excess of dimethyl sulphate (38 grams) was very slowly added; the oily drops rapidly disappeared on shaking and the liquid became appreciably hotter. After cooling, the mixture was extracted once with ether to remove unchanged dimethyl sulphate, then slightly acidified with sulphuric acid and evaporated to a small bulk. After removing the separated sodium sulphate and sodium methyl sulphate, the filtrate was evaporated with absolute alcohol and the residual syrup cooled in a desiccator. A white, crystalline substance was thus obtained which is exceedingly deliquescent, very soluble in water, and quite insoluble in

organic solvents. From these properties the substance is probably very similar to the trimethyl anhydro-salt, $C_6H_4\langle\overset{-}{SO_2}\overset{-}{NMe_3}\rangle O$, formed from sulphanilic acid (Griess, *Ber.*, 1879, 12, 2116), which has corresponding physical properties, but it has not yet been obtained in the pure state, a slight residue being left after ignition. When the substance was heated for five hours with concentrated aqueous potassium hydroxide, methyl alcohol was formed, which was removed by distillation and recognised by converting it into methyl salicylate. From the cold alkaline solution, crystals of potassium dimethyl- β -naphthylamine-8-sulphonate were obtained and were purified by repeated crystallisation from water. The salt forms white, anhydrous, lustrous crystals, and is easily soluble in water or alcohol.

0.2775 gave 0.0844 K_2SO_4 . $K = 13.76$.

$C_{12}H_{12}O_3NSK$ requires $K = 13.5$ per cent.

Dimethyl- β -naphthylamine-8-sulphonic acid was obtained by adding concentrated hydrochloric acid to a saturated solution of the potassium salt. The precipitate was recrystallised from hot dilute hydrochloric acid and then twice from water. The acid forms anhydrous white needles and melts at 244° . It is sparingly soluble in cold water, but dissolves readily in hot water or alcohol; the solutions exhibit a beautiful blue fluorescence. The acid does not form a nitroso-compound.

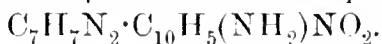
0.1988 gave 10.1 c.c. moist nitrogen at 18° and 764.4 mm. $N = 5.8$.

0.4804 required 19.25 c.c. $N/10$ KOH. $M.W. = 249.5$.

$C_{12}H_{13}O_3NS$ requires $M.W. = 251$ and $N = 5.6$ per cent.

Behaviour with Diazonium Salts.—A solution containing 0.21 gram of *p*-toluidine was diazotised and added to the solution of the equivalent quantity of dimethyl- β -naphthylamine-8-sulphonic acid. By the addition of excess of sodium acetate, a red colour was developed which did not become intensified after five hours. The solution was therefore slowly poured into a cold alkaline solution of β -naphthol, and the red precipitate of *p*-tolueneazo- β -naphthol was collected at the pump on a Gooch crucible, well washed with hot water, and dried at 116° . From the weight of the azo-compound, 0.48 gram, it was calculated that more than 91 per cent. of the diazonium salt had remained uncombined after an interval of five hours.

In a similar experiment with benzenediazonium chloride, 87 per cent. remained unchanged after the same interval of time.

p-Tolueneazo- β -amino-8-nitronaphthalene,

A solution containing 1.6 grams of *p*-toluidine was diazotised and added to 2.8 grams of 8-nitro- β -naphthylamine dissolved in 700 c.c. of water containing a small quantity of acetic acid. The mixed solutions became faintly turbid, and after the addition of excess of sodium acetate a bright red solution was produced, from which a bulky, flocculent precipitate slowly separated; this was collected, washed, and dried. The substance is very sparingly soluble in organic solvents of low boiling point, and is therefore best purified by crystallisation from ethyl benzoate, from which it separates in reddish-brown needles with a green reflex. The crystals were washed with alcohol to remove the last traces of the solvent, and dried at 100°.

0.1301 gave 22.2 c.c. moist nitrogen at 23° and 740 mm. $\text{N} = 18.2$.

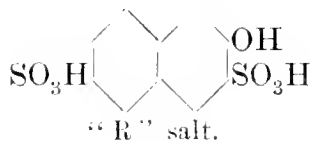
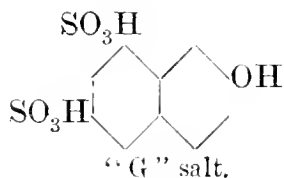
$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_4$ requires $\text{N} = 18.3$ per cent.

The substance melts at 253°, develops an intense reddish-violet coloration with concentrated sulphuric acid, is not decomposed by cold concentrated hydrochloric acid, and does not form an acetyl derivative when heated with acetic anhydride in glacial acetic acid solution.

In the hope of obtaining a diazoamine by the use of a diazo-complex of large molecular volume, 8-nitro- β -naphthylamine (2 mols.) was treated with nitrous acid (1 mol.), but after the addition of sodium acetate a dark red precipitate was obtained which gave an intense blue coloration with sulphuric acid, and was not decomposed by cold hydrochloric acid; this was evidently therefore an aminoazo-compound, but was not further examined.

Rate of Reaction of "G" and "R" Salts with Diazonium Salts.

The different behaviour of these isomeric β -naphthol disulphonic acids,



towards diazonium compounds has long been known, but hitherto a strict comparison between the action of the salts under identical conditions has not been instituted. For this purpose a dilute alkaline solution of "G" or of "R" salt was brought into contact with the solution of the diazonium salt, and after definite intervals of time the

amount of uncombined *p*-toluenediazonium chloride was estimated in the form of *p*-tolueneazo- β -naphthol, as previously described.

In the first set of experiments, the following solutions were prepared:

(a) 3.48 grams of "G" salt and 3.5 grams of sodium carbonate in 200 c.c. of water.

(b) A solution of "R" salt of the same composition.

(c) 1.07 grams of *p*-toluidine and 6.5 c.c. of concentrated hydrochloric acid were diazotised with 0.69 gram of sodium nitrite, and the resulting solution made up to 250 c.c.

(d) Five grams each of β -naphthol and potassium hydroxide dissolved in 200 c.c. of water.

The experiments were carried out at 0° in the following way. Fifty c.c. of (a) or of (b) and 50 c.c. of (c) were thoroughly mixed, and after definite intervals of time 10 c.c. of the mixture were run into 50 c.c. of (d); the precipitate of *p*-tolueneazo- β -naphthol was collected, washed, and weighed. The results are expressed in the table, in which the second and third columns give the weight of *p*-tolueneazo- β -naphthol and the percentage of uncombined diazonium salt respectively for the solution containing the "G" salt, and the fourth and fifth columns the corresponding data for the "R" salt.

Time in minutes.	II.	III.	IV.	V.
0	0.0486	100.0	0.0486	100.0
2	0.0480	98.8	0.0032	6.6
5	0.0466	95.8	nil	
10	0.0415	84.4	,,	
20	0.0402	82.8	,,	
120	0.0354	72.8	,,	
14 hours	0.0190	39.0	,,	

In this series of experiments a viscous precipitate separated directly the solutions of the "R" salt and of the diazonium chloride were mixed, a proceeding which may have tended to vitiate the comparison. A second series was therefore performed with the following solutions:

(a) 3.48 grams of "G" salt in 500 c.c. of water.

(b) 3.48 grams of "R" salt in 500 c.c. of water.

(c) A solution made by diazotising 1 gram of *p*-toluidine and diluting to 500 c.c.

(d) A solution containing 0.0144 gram each of β -naphthol and potassium hydroxide per c.c.

Two hundred c.c. of (a) or of (b) were mixed with 30 c.c. of *N*-sodium carbonate solution and 200 c.c. of (c). A precipitate did not separate. After definite intervals 50 c.c. of the mixed solutions were added to 20 c.c. of (d) and the precipitated azo-compound treated as before.

Time in minutes.	II.	III.	IV.	V.
0	0.1131	100.0	0.1134	100.0
5	0.1062	94.0	0.0143	12.6
15	0.0956	84.5	nil	
180	0.0873	77.2	,,	
24 hours	0.0351	31.0	,,	

These figures indicate very clearly the steric hindrance produced by the presence of the SO_3H group in position 8.

Sodium 1-Bromo- β -naphthol-8-sulphonate.

A cold saturated aqueous solution containing 25 grams of sodium β -naphthol-8-sulphonate (1 mol.) was slowly treated with 16 grams (1 mol.) of bromine. The halogen quickly disappeared, and the solution became warm and acquired a dark green colour which changed to reddish-brown. After several hours the brown precipitate, which showed an acid reaction, was collected, washed once with a strong solution of sodium hydroxide, and thrice recrystallised from water, whereby the substance was obtained in colourless, glistening leaflets which turn brown in the air.

1.2106 lost 0.1667 at 110° . $\text{H}_2\text{O} = 13.8$.

$\text{C}_{10}\text{H}_6\text{O}_4\text{BrSNa} \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 14.2$ per cent.

0.3689, dried at 110° , gave 0.2104 AgBr. $\text{Br} = 24.3$.

$\text{C}_{10}\text{H}_6\text{O}_4\text{BrSNa}$ requires $\text{Br} = 24.6$ per cent.

Behaviour with p-Toluenediazonium Chloride.—A solution containing 0.9 gram of the anhydrous salt was treated with the diazonium chloride obtained from 0.3 gram of *p*-toluidine. After the addition of sodium acetate the mixture was thoroughly stirred. The colour of the solution did not change for several hours, when it became red. After five minutes, three hours, and nine hours respectively, 25 c.c. of the solution were added to an alkaline solution of β -naphthol, and the weights of the washed and dried *p*-tolueneazo- β -naphthol were:

0.1230	gram	after 5 minutes
0.1232	,,	3 hours
0.1226	,,	9 "

Evidently the group in position 8 had completely hindered the elimination of the halogen by the diazonium salt. For comparison, sodium 1-bromo- β -naphthol-6-sulphonate was treated with *p*-toluene diazonium chloride, when, after the addition of sodium acetate, a dark red solution was immediately obtained, from which excess of sodium acetate precipitated the sodium salt of an azo-compound which was free from halogen. The free acid was dark red in colour, whereas

p-tolueneazo- β -naphthol-6-sulphonic acid prepared directly from its constituents forms bright red crystals with a green reflex. This difference, together with the fact that benzeneazo- β -naphthol, obtained from 1-bromo- β -naphthol and benzenediazonium chloride, is very difficult to crystallise, makes it advisable to examine more thoroughly the elimination of the halogen from brominated naphthols by diazonium salts.

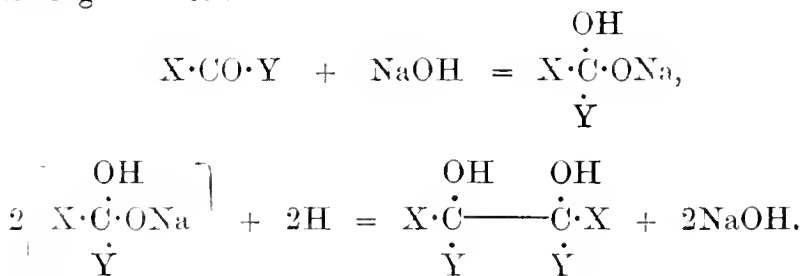
I desire to express my indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expense of this investigation.

EAST LONDON COLLEGE.

CXLIX.—*Electrolytic Reduction. I. Aromatic Aldehydes.*

By HERBERT DRAKE LAW.

THE first account of the reduction products of the aromatic aldehydes obtained by means of an electric current was given by Kaufmann (*Zeit. Elektrochem.*, 1895, 2, 365), who showed that benzaldehyde in a sodium bisulphite solution yielded a mixture of a small quantity of hydro- and isohydro-benzoin at the cathode. At a later date the same author stated that a much better yield was obtained when alcoholic solutions were used, employing sodium hydroxide as electrolyte (*Zeit. Elektrochem.*, 1898, 4, 461). Benzoin, benzil, and acetophenone all gave products similar to the above, the reaction taking place presumably in the following manner:



In 1902, Elbs and Brand (*Zeit. Elektrochem.*, 8, 784) obtained similar results with a number of ketones, but here the reaction often proceeded a stage further and the alcohol corresponding to the aldehyde was produced.

In the present work the first experiments were conducted with

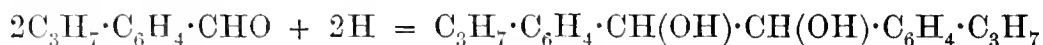
benzaldehyde in alcoholic solutions, using potassium hydroxide as the electrolyte. An almost theoretical yield of *isohydro*- and *hydro*-benzoin was obtained together with a very small quantity of resinous matter, which was, however, not sufficient to interfere with the reaction. The introduction of such groups as $-\text{OH}$, $-\text{OCH}_3$, $\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CH}_2$ into the benzene nucleus was found also to interfere to no considerable extent with the main reaction. Such aldehydes as furfural and cinnamaldehyde, which contain an unsaturated carbon atom, yielded nothing but a resinous product. The latter agrees with the anodic phenomenon and confirms the statement already made (*Trans.*, 1906, 89, 1437), that unsaturated aldehydes polymerise under the influence of an electric strain. Benzoin, piperonyloin, anisoin, and cuminoil all yield similar products, of which tetraphenylerythritol may be taken as a type. The appearance of such substances as anisil is remarkable, however, and no explanation is given.

Description of the Apparatus.

Throughout this research the same form of apparatus was used. The cathode compartment consisted of a cylindrical porous pot, having a capacity of 120 c.c. This was thoroughly cleaned by forcing first a dilute solution of sodium hydroxide and then dilute sulphuric acid through the walls to remove the soluble metallic impurities. Such a porous pot was fitted with a treble-bored rubber stopper carrying a dropping funnel, a short delivery tube, and a short glass tube to hold the electrode. In each case the cathode was bent in the form of a cylinder, and was fixed in position by means of sealing-wax; it had an area of 17.5 sq. cm. on one side. The hydrogen escaping from the apparatus was conducted to a graduated measuring cylinder inverted over water, and the volume read off from time to time. The anode compartment was a beaker about 10 cm. deeper than the porous pot, containing a stout platinum wire to act as anode. Three such sets of apparatus were coupled in series with an adjustable rheostat and twelve accumulators. One piece of apparatus was used as a hydrogen coulombmeter and the other two for reduction purposes, one being a duplicate of the other. In this way the total hydrogen reacting at the cathode could be measured from the difference in the water levels of the coulombmeter and the reduction apparatus. In many cases the product was precipitated during the experiment on to the cathode, but did not interfere with the reaction as is the case in acid solutions.

Cuminaldehyde.

The cathode solution measured 75 c.c. and contained 5 grams of cuminaldehyde, 50 c.c. of absolute alcohol, 5 per cent. of potassium hydroxide, the remainder being distilled water. The cathode was either polished nickel or platinum, and the current of 1 ampere was continued for two to three hours. At the end of the experiment 360 c.c. of hydrogen had been absorbed, whilst the theoretical amount calculated from the equation



is 375 c.c. No solid had separated and the cathode solution was, therefore, precipitated by water. The product weighed nearly 5 grams. This was washed with hot light petroleum and filtered from the insoluble portion. The latter weighed 2 grams, and after crystallisation from heavy petroleum melted finally at 137° . This was found to be hydrocuminoin. The portion soluble in light petroleum was recovered and recrystallised several times and in each case the final product was the above substance melting at 137° . The residue always melted at $90\text{--}92^\circ$, but continued to yield a further quantity of the substance of high melting point on further purification. This may have been due to the gradual conversion of the one into the other during the process of crystallisation. The substance melting at $90\text{--}92^\circ$ gave the following result on analysis:

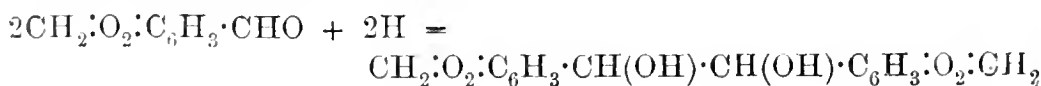
0.1017 gave 0.2990 CO_2 and 0.0757 H_2O . $\text{C} = 80.14$; $\text{H} = 8.27$.

$\text{C}_{20}\text{H}_{26}\text{O}_2$ requires $\text{C} = 80.53$; $\text{H} = 8.72$ per cent.

This is, therefore, probably *isohydrocuminoin* containing a little hydrocuminoin. In addition to these two substances there was formed also a small quantity of resinous matter which, on long standing, deposited a little more mixed product.

Piperonaldehyde.

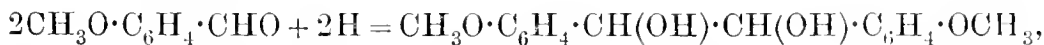
The solution in the cathode compartment contained 5 grams of piperonaldehyde, 38 c.c. of absolute alcohol, 5 per cent. of potassium hydroxide, and the whole was made up to 75 c.c. with water. The cathodes were either polished nickel or platinum. A current of 1 ampere was passed through this solution for three to four hours. At the end of that time a yellow solid had separated from the solution, which was then filtered. The amount of hydrogen absorbed during this process was 350 c.c., whilst that required by the equation



is 370 c.c. It was expected, therefore, that an almost theoretical yield of hydropiperonyloin had been obtained. The part remaining in the alcoholic solution was precipitated by means of water and filtered. The two portions obtained in this way weighed almost 5 grams and were present in equal quantities. The yellow solid which had separated during the experiment was crystallised twice from amyl alcohol and the melting point was found to be 200° . This substance is soluble with difficulty in organic solvents, and is undoubtedly hydropiperonyloin, the melting point of which is given as 202° . The other portion was crystallised twice from benzene and the melting point was found to be 132° . This substance is therefore isohydropiperonyloin (m. p. 132°). Both the above compounds were first prepared by Fittig and Remsen (*Annalen*, 1871, 159, 130) by reducing piperonal with sodium amalgam.

Anisaldehyde.

The solution at the cathode contained 5 grams of anisaldehyde, 38 c.c. of alcohol, 5 per cent. potassium hydroxide, and the whole was made up to 75 c.c. with distilled water. The cathodes used were composed either of polished platinum or nickel. A current of 1 ampere was allowed to pass through the solution for two to three hours, at the end of which time 380 c.c. of hydrogen had been absorbed. According to the equation



410 c.c. are required, which is a very close agreement. At the end of the experiment, part of the product had separated and was removed by filtration from the alcoholic solution. The latter was poured into water to precipitate the soluble matter. These two portions were almost equal in weight, the total amount being 5 grams. The insoluble portion was crystallised twice from alcohol, when the melting point was found to be 170° . The other part, after being crystallised from a mixture of alcohol and water, and finally from benzene, melted at 113° . These two substances were therefore hydroanisoin (m. p. 168°) and isohydroanisoin (m. p. 110°) respectively (*Annalen*, 1871, 159, 130).

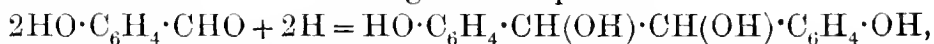
Vanillin.

In this case, it was quite essential to prevent the free access of air from the cathode compartment and to keep the temperature as low as possible with running water, otherwise the product was entirely resinous. The cathode solution measured 75 c.c., and contained 5 grams of vanillin and 5 per cent. of potassium hydroxide, the remainder being water. A current of 1 ampere was passed through this solution for two and a half to three hours, at the end of which time 380

c.c. of hydrogen had been absorbed, whilst only 370 c.c. were necessary for the production of hydrovanilloin. The cathodes, which were similar to those used in previous experiments, always became covered with a dark brown deposit. The cathode solution was acidified with hydrochloric acid and allowed to stand until no more crystals separated, and a product, amounting to 80 per cent. of the theory, was obtained. The crude substance always contained a quantity of resin, which was removed by washing with chloroform. The insoluble residue melted at 222° and was *hydrovanilloin*. No definite product was obtained from the resin, but it is probable that it contained some isomeric compound. The yield of pure hydrovanilloin was 45 per cent. of the theory.

Salicylaldehyde.

The product in this case is even more readily influenced by changes of the conditions than is vanillin. It is absolutely essential to exclude the free access of air during the experiment, and the best results were obtained with low current densities. The cathode solution contained 5 grams of salicylaldehyde and 5 per cent. of potassium hydroxide, the total volume of the solution being 75 c.c. In this case, no alcohol was required, the substance being readily soluble in the alkaline solution. A current of 0.2 ampere was used, and the whole apparatus was kept cool by means of cold water. The experiment was allowed to proceed until no more hydrogen was observed and was complete in eight to nine hours. According to the equation



410 c.c. of hydrogen are required to complete the reaction, whilst in an actual experiment 460 were absorbed. The mixture was diluted with water and several grams of potassium bicarbonate added. The solution was kept cool with ice or cold water and precipitated with dilute hydrochloric acid. It was found necessary to proceed in this manner, as acids stronger than carbonic acid caused the substance to darken considerably during the precipitation, and at the same time effected no separation of the two substances formed. The first portion precipitated was a white, amorphous powder which could not be obtained in a crystalline state. It was purified by dissolving in sodium hydroxide and reprecipitating with hydrochloric acid. It begins to soften at 122° and chars at 147° without melting.

0.1004 gave 0.2490 CO_2 and 0.0561 H_2O . C = 67.91; H = 6.21.

$\text{C}_{14}\text{H}_{14}\text{O}_4$ requires C = 68.29; H = 5.70 per cent.

The substance is therefore *hydrosalicyloin*, or a mixture of *isohydro-* and *hydro-salicyloin*. The yield was 70 per cent. of the theory.

The solution on standing for several days deposited a further quantity of a substance which, on being crystallised from dilute

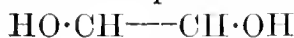
alcohol, melted at 113° . On analysis, the following results were obtained :

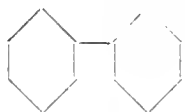
0.1015 gave 0.2950 CO_2 and 0.0481 H_2O . $\text{C} = 79.26$; $\text{H} = 5.26$.

$\text{C}_{14}\text{H}_{12}\text{O}_2$ requires $\text{C} = 79.24$; $\text{H} = 5.66$ per cent.

A molecular weight determination by the freezing-point method in benzene solution gave the values 197 and 196.

A compound of the above formula requires $\text{M.W.} = 212$, which agrees fairly closely with the experimental result. The substance, which is insoluble in caustic alkalis, is readily attacked by bromine, evolving dense fumes of hydrobromic acid. In this respect it behaves like the secondary alcohols of the benzene series, and from the method of preparation such a compound was to be expected. It is therefore



probably 9 : 10-dihydroxyphenanthrene,  .

Reactions similar to these will be investigated in the near future.

Furfurol.

This substance in alkaline solutions was completely converted into a semi-solid, tarry mass very closely resembling the product obtained by electrolytic oxidation. In sulphuric acid solution the mixture was often oily in appearance, and contained considerable quantities of furan carbinol, the main portion, however, always being of a resinous nature.

Cinnamaldehyde.

This unsaturated compound behaves exactly like furfurol, the main product being tar.

Anisoin.

Five grams of this substance were dissolved in 55 c.c. of alcohol, and the whole was made up to 70 c.c. with water. Sufficient potassium hydroxide dissolved in 5 c.c. of water was added to give a 5 per cent. solution. Complete solution was effected only by keeping the mixture warm, and then a beautiful purple solution was obtained. A current of 1 ampere was passed through this solution for eight hours, at the end of which time the reaction was complete. The cathodes used were either platinum or nickel. When the experiment was finished, part of the product had separated from the solution and was removed by filtration. This insoluble portion was dissolved in pyridine and fractionally precipitated. In this manner a white, flocculent mass was obtained which gave the following result on analysis :

0.1020 gave 0.2630 CO_2 and 0.0580 H_2O . $\text{C} = 70.32$; $\text{H} = 6.32$.

$\text{C}_{32}\text{H}_{34}\text{O}_8$ requires $\text{C} = 70.33$; $\text{H} = 6.23$ per cent.

The substance is therefore *tetra-anisylerythritol*, possessing the constitution

$$\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\overset{\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4}{\underset{\text{C}_6\text{H}_4\cdot\text{OCH}_3}{\text{C}}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3}$$

The portion still in solution was precipitated by pouring into water, when a yellow solid was obtained. This was washed several times with small quantities of boiling methyl alcohol, and from the first of these washings crystals of a yellow substance separated on cooling, but the latter portions gave a semi-solid mass which was only partially crystalline. These crystals melted sharply at 132° , and on analysis :

0.1016 gave 0.2667 CO_2 and 0.0512 H_2O . $\text{C} = 71.40$; $\text{H} = 5.58$.

Molecular weight in benzene solution = 251.

$\text{C}_{16}\text{H}_{14}\text{O}_4$ requires $\text{C} = 71.11$; $\text{H} = 5.18$ per cent., and M.W. = 270.

The substance is therefore anisil (m. p. 133°). The formation of this diketone at the cathode is difficult to explain ; it is certainly not a primary product of the reduction.

The semi-solid mass was not treated further as no crystalline product could be obtained. On long standing, further crystals of anisil were deposited, but these could not be removed completely.

The insoluble portion left after the washing with hot alcohol amounted to 35—40 per cent. of the whole.

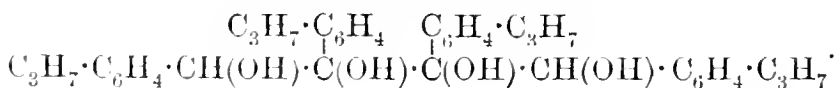
Cuminoin.

Five grams of this substance were dissolved in 55 c.c. of alcohol to which 7.5 c.c. of a 50 per cent. solution of potassium hydroxide were added, and the whole was made up to 75 c.c. with water. A purple solution was obtained which was kept warm in order to prevent part of the cuminoin from crystallising out. The cathode was composed of either polished platinum or nickel, and a current of 1 ampere was passed until no more hydrogen was absorbed. The reduction was complete in two to three hours, when part of the product had been precipitated from the solution. This portion, which amounted to 40 per cent. of the cuminoin employed, was dissolved in a mixture of hot alcohol and pyridine, and precipitated fractionally with water. In this manner a white, flocculent product was obtained, which, after drying on a porous plate, formed a white, semi-transparent, brittle mass resembling cellulose in appearance.

0.1010 gave 0.3030 CO_2 and 0.0898 H_2O . $\text{C} = 81.02$; $\text{H} = 8.88$.

$\text{C}_{40}\text{H}_{50}\text{O}_4$ requires $\text{C} = 80.81$; $\text{H} = 8.42$ per cent.

This substance is, therefore, *tetracuminylerythritol*, possessing the formula



It is soluble only in acidic and basic organic solvents, from which it can be precipitated as an amorphous powder melting at 210—212°. The filtrate from the crude product was poured into water, and 2 grams of a viscid, semi-solid mass were obtained. This was dissolved in alcohol, which was allowed to evaporate very slowly, and the solid matter separated from the resinous part. The former was then carefully crystallised from a mixture of pyridine and water, when a white, crystalline substance was obtained melting sharply at 81°. This proved to be cuminil (m. p. 84°), but the yield was very small.

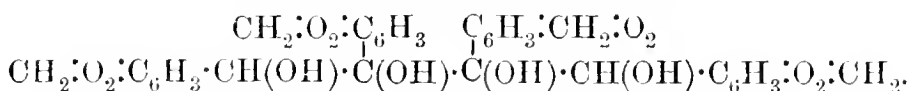
Piperonyloin.

Five grams of this substance were dissolved in 55 c.c. of alcohol, to which were added 7.5 c.c. of a 50 per cent. solution of potassium hydroxide. The mixture was then made up to 75 c.c. with distilled water, and warmed to keep the whole of the piperonyloin in solution. As the experiment proceeded, however, the whole remained dissolved, as the product is very soluble in alcoholic potash. The fresh solution was violet, but after the experiment was finished this had changed to yellow. When the reduction, which required from two to three hours, was complete, the whole was poured into water to precipitate the product, which amounted to 4.5 grams. This was dried and extracted with ether. The residue was a white, amorphous mass, quite insoluble in neutral organic solvents, but readily soluble in acetic acid or pyridine. It was purified by dissolving in a mixture of pyridine and alcohol, from which it was precipitated on cooling as a white, flocculent precipitate (m. p. 203—205°), resembling cellulose in appearance; yield, 35 per cent. On analysis:

0.1035 gave 0.2432 CO₂ and 0.0433 H₂O. C = 64.08; H = 4.65.

C₃₂H₂₆O₁₂ requires C = 63.79; H = 4.32 per cent.

This substance is therefore *tetrapiperonylerythritol*,



The portion soluble in ether gave, on evaporation, a viscid, yellow substance, which on standing in a vacuum set to a hard, brittle mass.

This was evidently a mixture of at least two substances, and from its deep yellow colour, and by analogy to anisoïn and cuminoïn, it probably contains piperonil.

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CL.—*Electrolytic Reduction. II. Use of Electrodes.*

By HERBERT DRAKE LAW.

DURING some preliminary experiments it was observed that benzaldehyde is reduced almost entirely to hydro- and *isohydro*-benzoin on nickel, platinum, iron, and copper cathodes, the velocity of the reaction being about the same in each case. The potential of the metal, however, varied very considerably in each experiment, and also during the whole series. It was obvious, therefore, that some other influence was at work regulating these reactions. We may suppose that the entire reaction takes place in the immediate vicinity of the cathode, causing the neighbouring layer of solution to become almost free from benzaldehyde. The actual reduction probably takes place rapidly in comparison to the diffusion of the substance through the impoverished layer, and the latter process therefore determines the velocity of the reaction. Let C represent the concentration of the benzaldehyde in the bulk of the solution and C' that at the cathode. If $\frac{dc}{dt}$ represents the rate of diffusion, then the following relation holds good when C' is small:

$$\frac{dc}{dt} = KC'.$$

This also represents the rate of hydrogen absorption. If H is the total amount of hydrogen that may react and h the quantity used after a time t , the following equation results after substitution and integration:

$$\frac{1}{t} \log \frac{H}{H-h} = K'$$

or

$$\frac{1}{Hc} \log_{10} \frac{H}{H-h} = K,$$

where Hc represents the hydrogen liberated in the coulombmeter.

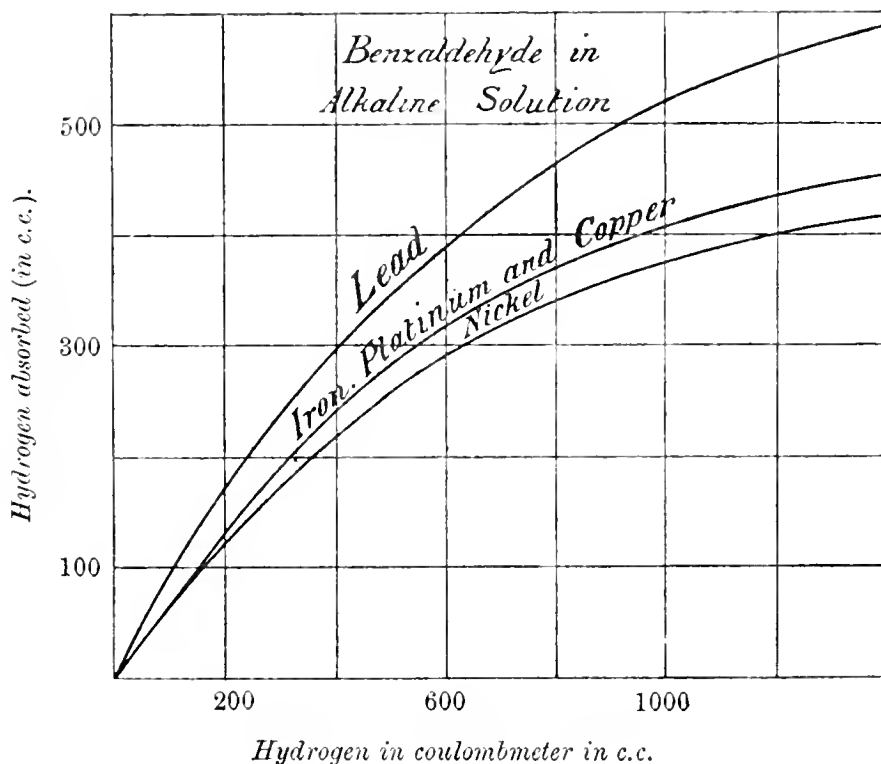
For nickel, platinum, copper, and iron, the following results were obtained:

<i>Nickel.</i>				<i>Platinum and Copper.</i>			
Hc .	H .	$H-h$.	K .	Hc .	H .	$H-h$.	K .
170 c.c.	560 c.c.	450 c.c.	559	330 c.c.	560 c.c.	360 c.c.	580
440	315 ..	566	585	245 ..	613
635	245 ..	565	800	180 ..	616
1110	170 ..	466	1080	140 ..	559
1290	155 ..	465	1370	90 ..	580
1420	140 ..	424				

<i>He.</i>	<i>Fe.</i>	<i>Iron.</i>	<i>K.</i>
200 c.c.	560 c.c.	425 c.c.	599
355 "	"	340 "	519
700 "	"	210 "	608
1000 "	"	150 "	572
1465 "	"	95 "	526
1640 "	"	80 "	516

In these results the order of magnitude of K has not been taken into account, but the three series are comparable among themselves.

FIG. 1.



The figures are taken from the curves in Fig. 1. The constant value of K proves that the velocity of the reaction is independent of the potential of the cathode. This is true, however, only when the factor C' may be neglected. In a previous paper (Chapman and Law, *Analyst*, 1906, 31, 3) it was shown that the following relation holds good for the reduction of arsenious oxide :

$$M_{\text{AsH}_3} \propto K_{\text{As}} \times P_{\text{H}},$$

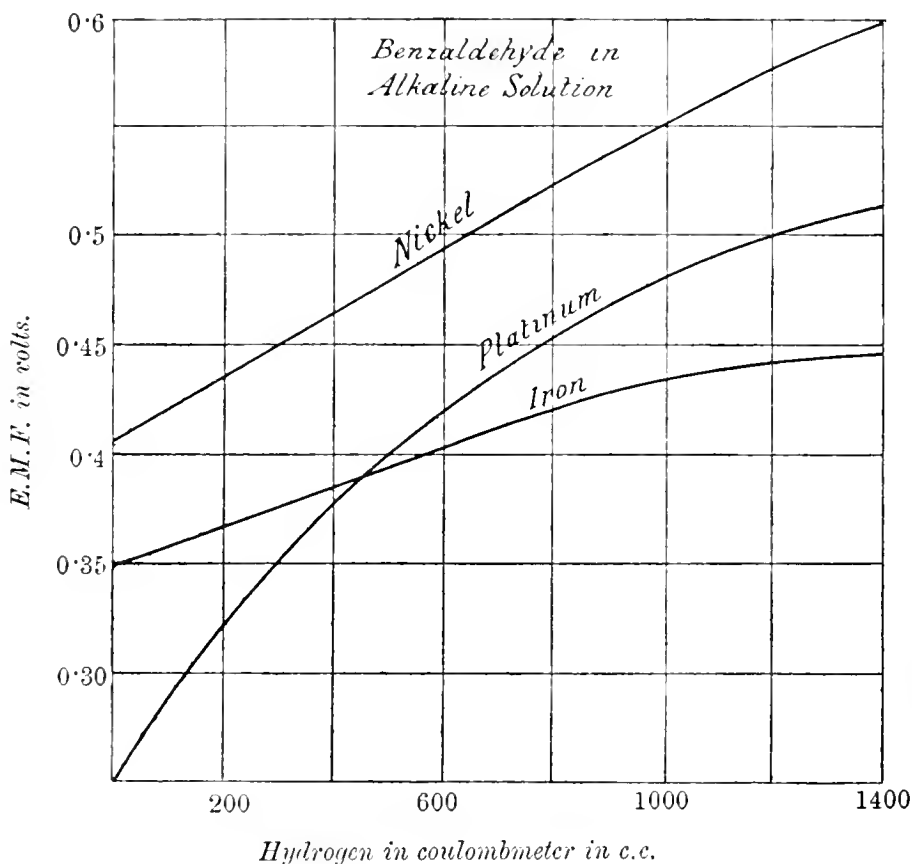
which may be expressed as

$$C - C' \propto 2C' \times P_{\text{H}}$$

for benzaldehyde, P_{H} being a factor dependent on the potential of the

cathode. As C' is very small in general, an increase in the factor P_H is practically without influence in the velocity equation. If, however, the cathodic potential becomes very small, and consequently the factor P_H also, C' gradually approaches C in value. The velocity of the reaction then decreases and finally becomes nil, when C is equal to C' . Thus, on iron and platinised platinum electrodes free from catalytic effects, the reduction taking place is very small (Fig. 5). The above equations refer to stationary electrodes free from disturbing influences, but the hydrogen liberated at the cathode agitates

FIG. 2.



the solution, and the reduction takes place more rapidly than the above relation allows, or, in other words, the constant factor increases at first and decreases towards the end of the experiment. This is to be noticed on all four electrodes mentioned in the foregoing table. The same phenomenon is recorded by Farup (*Zeit. physikal. Chem.*, 1906, **54**, 640) for the reduction of azobenzene with rotating cathodes. As the stirring becomes greater, the rate of reduction increases until a stage is reached independent of the diffusion.

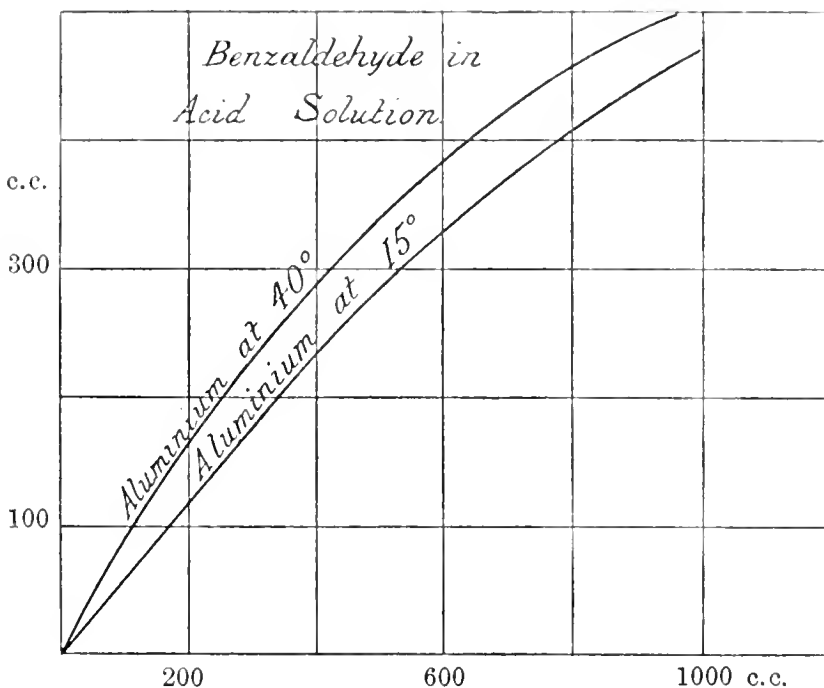
As the potential of the cathode increases, the reduction becomes more and more complex. Thus, in the case of lead (Fig. 1), the curve

has risen higher than is required for the formation of hydrobenzoin, due to the formation of a small quantity of benzyl alcohol; more resin also is produced.

The rate of diffusion increases with rising temperature, causing an acceleration of the reduction velocity. This may be seen in the case of aluminium cathodes (Fig. 3). At the higher temperature more resin is also formed, which interferes with the reaction and causes the curves to rise more slowly than they would do otherwise (Figs. 1 and 3).

Such influences as do not materially affect the rate of diffusion or the potential of the cathode have little or no action on the velocity of

FIG. 3.

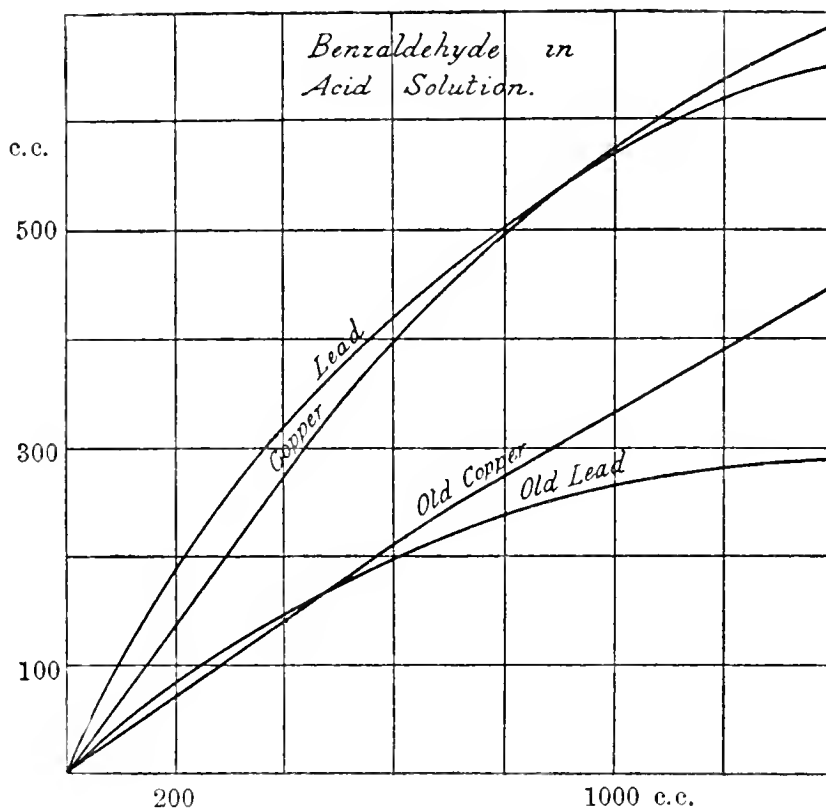


the reduction. Thus, a change in the current density produces only a very small effect on the factor $\frac{dh}{dIc}$ (Fig. 6).

The results obtained above refer chiefly to alkaline solutions, where the reactions are moderately simple. When sulphuric acid is substituted, the resin formation is greatly increased. The production of these complex substances is greatest on metals having a high super-tension, as in the case of lead. As the potential of the electrode falls, the quantity of resin formed diminishes, until on copper hardly any is produced. Aluminium and platinum occupy an intermediate position. The reaction also proceeds further than in alkaline solutions, benzyl alcohol being also obtained (Fig. 4). In the case of lead, the

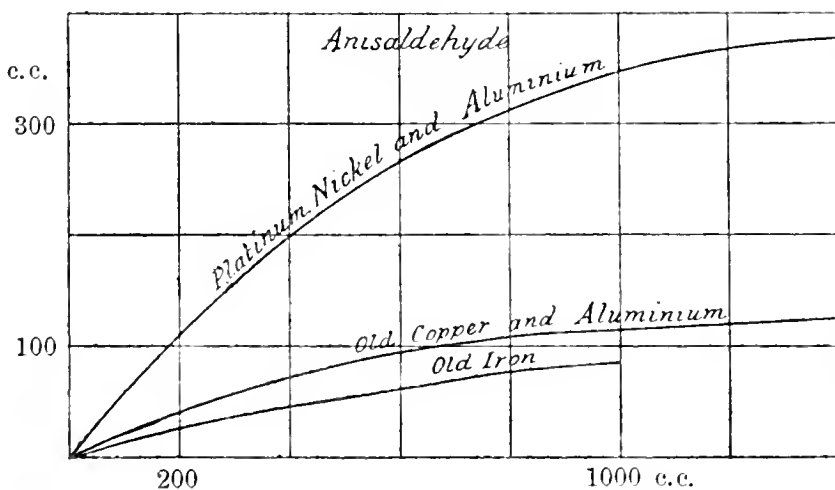
velocity of the reaction proceeds rapidly at first, but eventually falls below that of copper in spite of the higher potential of the former; at

FIG. 4.



the same time, the lead electrode becomes thickly coated with resin, which screens the action (Fig. 4). The reducing efficiency of an

FIG. 5.



electrode decreases greatly after a few experiments. The curves marked "old" (Figs. 4 and 5) were obtained in the same manner

as the others, but old electrodes were used. The straight curve obtained in the case of "old copper" was due to the gradual recovery of the reducing efficiency of the electrode caused by an increase of the potential. This phenomenon occurs very often with electrodes whose potential is below the normal value. It was noticed most often in electrolytic iron, aluminium, and nickel, the potential being sometimes too low to reduce benzaldehyde at the commencement of the experiment. This is caused in all probability by metallic impurities of low supertension which diffuse into or become coated with the metal constituting the bulk of the electrode as the experiment proceeds. If such cathodes, which have recovered in this manner, are exposed to the oxidising action of the air, they again become inefficient for reduction purposes, due to this etching and consequent exposure of the impurities. Tafel also has recorded similar results.

EXPERIMENTAL.

The experiments were all conducted in the manner already described in the preceding paper. The results were plotted in the form of curves, the ordinates representing the hydrogen absorbed by the aldehyde, and the abscissæ giving the hydrogen of the coulombmeter. The potential of the electrodes was measured by the usual Wheatstone bridge arrangement against a hydrogen half element. In the curves representing these, the ordinates show the measured potential ($H=0.00$ volt), whilst the abscissæ remain as before.

Anisaldehyde.

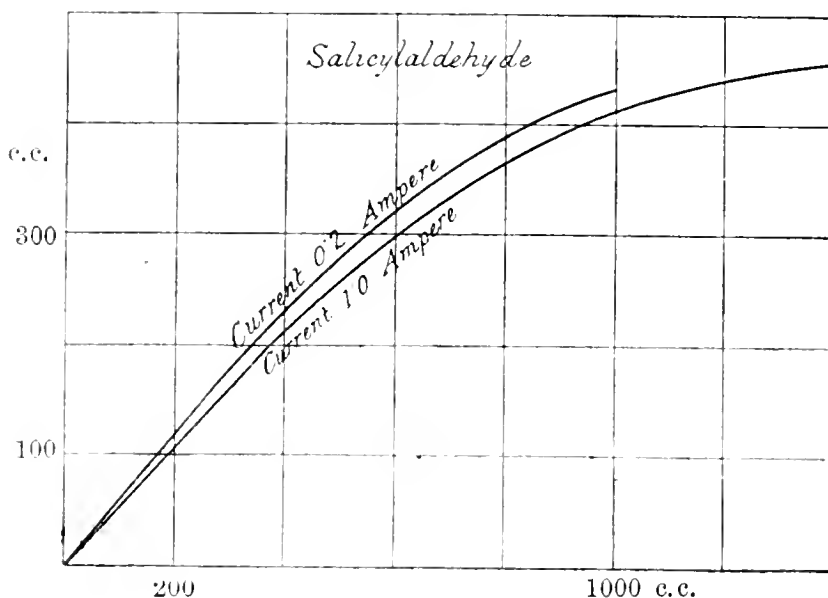
The results obtained with anisaldehyde agreed with the previous ones (see preceding paper), but fewer complications occurred. In both acid and alkaline solutions a mixture of hydro- and isohydro-anisoin nearly free from resin was obtained (Fig. 5). Only as the temperature of the solution rose was any considerable amount of resinous matter formed. Old electrodes behave in exactly the same manner as the ones already described (Fig. 5). This curious behaviour is largely due to a small platinum deposit, and may completely change the character of the reaction (Law, *Trans. Faraday Soc.*, 1906, 1, 72).

Salicylaldehyde.

In this case a very small increase of temperature caused the product to be entirely resinous in character. Only very low current densities could be employed, due, no doubt, to the decreased heating effect

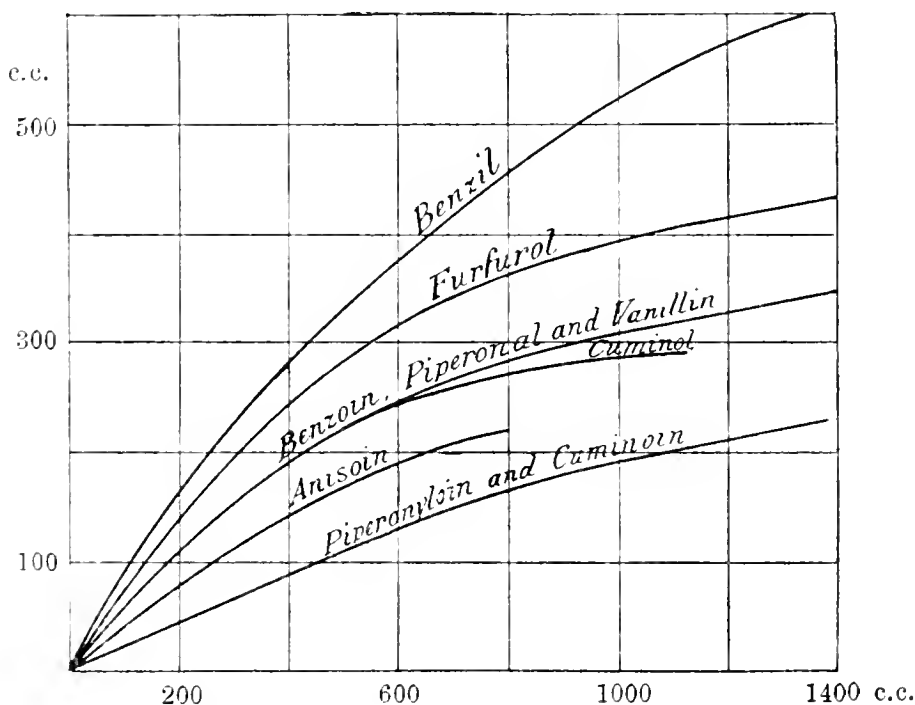
(Fig. 6). Alkaline solutions were used. In each experiment 25 per cent. more hydrogen was absorbed than the simple production of

FIG. 6.



hydrosalicyloin requires, the phenolic radicle also having been attacked. Changes of concentration in the electrolyte between 5 and 10 per cent.

FIG. 7.



produced hardly any effect on the velocity of the reaction, exactly as is the case with other aldehydes.

Other Aldehydes.

These experiments were all conducted in alkaline solutions, except in the case of furfurol, and the results are reproduced in Fig. 7. In each case these were logarithmic functions of the hydrogen in the coulombmeter. Thus, in the case of benzil, the following result was obtained.

<i>Hc.</i>	<i>H.</i>	<i>H-h.</i>	<i>K.</i>
400 c.c.	800 c.c.	530 c.c.	449
600 „	„	430 „	449
800 „	„	350 „	445
1000 „	„	280 „	445
1400 „	„	190 „	440

The remarkably constant value of *K* is due, no doubt, to the increased velocity of the reaction. This calculation is based on the assumption that the product is tetraphenylerythritol, which is nearly the case in potassium hydroxide solution.

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CLI.—*Some Derivatives of 2- and 3-Phenanthrol.*

By HERBERT HENSTOCK.

THE primary object of this research was to prepare and condense together two molecules of a phenanthrol derivative, water being eliminated according to the scheme :



The method which was tried for the preparation of the phenanthrol consisted in heating the 9- or 10-diazo-compound with water, but this failed, as is explained in the experimental portion of the paper, so that the initial idea could not be carried out. Neither the 2- nor the 3-ethoxyphenanthrene diazo-compounds could be converted into the corresponding ethoxyphenanthrols, and when a methoxy-compound was prepared in like manner it proved even more refractory.

This being the case, the diazo-compounds themselves were isolated and proved very interesting; they are both pale yellow, flocculent substances which are very difficult to obtain in a crystalline condition, and resemble each other in most respects. They differ, however, in

their behaviour under the action of heat; whilst the 2-compound is fairly stable even in alkaline solution, the 3-compound is decomposed at once on boiling, or in the cold if the solution is previously rendered alkaline.

EXPERIMENTAL.

2-Phenanthryl Ethyl Ether.

Fifteen grams of 2-phenanthrol were dissolved in a solution of 30 grams of potassium hydroxide in 250 c.c. of water and the solution well cooled. To this were added 20 grams (1.5 mols.) of diethyl sulphate, the mixture being well shaken at frequent intervals and allowed to stand overnight. It was then poured into about 1500 c.c. of water, which was well stirred, and the whole allowed to stand for half an hour. The ether was precipitated as a white, sandy powder, which was separated and dried. The yield was 17 grams. On recrystallising from glacial acetic acid, the substance was obtained in white, shining leaflets which melt at 112° . An almost quantitative yield can be obtained by working with cold solutions.

The substance is easily soluble in ether, benzene, light petroleum, or chloroform, sparingly so in alcohol or glacial acetic acid, and insoluble in water.

0.1230 gave 0.3890 CO_2 and 0.0710 H_2O . $\text{C} = 86.26$; $\text{H} = 6.42$.

$\text{C}_{16}\text{H}_{14}\text{O}$ requires $\text{C} = 86.47$; $\text{H} = 6.30$ per cent.

Nitration of the Ether.

Ten grams of recrystallised 2-phenanthryl ethyl ether were dissolved by warming in 350 grams of glacial acetic acid, and the solution cooled; concentrated nitric acid was then added until a slight permanent precipitate remained. On allowing the solution to stand, the mononitro-derivative was slowly precipitated as a pale yellow, amorphous powder. Yield 7.4 grams. Recrystallised from petroleum of high boiling point, it gave long, slender, pale yellow needles, melting at $157\text{--}158^{\circ}$.

On diluting the filtrate with a large quantity of water, a further quantity (2.5 grams) was obtained.

10-Nitro-2 phenanthryl ethyl ether, $\text{NO}_2 \cdot \text{C}_{14}\text{H}_9 \cdot \text{OEt}$, dissolves easily in ether, benzene, or chloroform; light petroleum is, however, much the best solvent for recrystallisation purposes.

A much larger quantity of nitric acid is required in the preparation of this substance than in the case of the nitro-derivative of the 3-series.

0.2100 gave 10.2 c.c. nitrogen at 14° and 727 mm. $\text{N} = 5.45$.

$\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}$ requires 5.24 per cent.

10-Amino-2-phenanthryl Ethyl Ether, $\text{NH}_2 \cdot \text{C}_{14}\text{H}_8 \cdot \text{OEt}$.

Ten grams of the nitro-compound were heated with 50 grams of granulated tin and 300 c.c. of fuming hydrochloric acid for one and a half hours, until the yellow colour had disappeared. The liquid was then decanted from any undissolved tin, which was washed twice with hydrochloric acid to remove any adhering substance. The solution was then cooled, the amino-hydrochloride separated, washed with cold water, and dissolved by heating in about a litre of water. On rendering alkaline, the free base was precipitated as a white, flocculent mass, which was separated and dried. Yield, 8 grams.

On recrystallisation from petroleum of high boiling point, slender, colourless needles were obtained, melting at 127° .

0.1305 gave 7.2 c.c. nitrogen at 20° and 730 mm. $\text{N} = 6.05$.

$\text{C}_{16}\text{H}_{15}\text{ON}$ requires 5.90 per cent.

Sodium-2-ethoxy-10-diazophenanthrene Sulphate,

One gram of the foregoing amino-derivative was dissolved in about 100 c.c. of dilute sulphuric acid and the solution cooled to about 7° , when crystals of the sulphate appeared. A slight excess of a dilute solution of sodium nitrite was added, and the resulting pale yellow solution filtered, saturated with common salt, and allowed to stand some hours in a cool place, when a pale yellow, flocculent precipitate was obtained, which was separated and dried. To purify the substance it was dissolved in cold water and reprecipitated by saturating the solution with salt. Yield, 1.2 grams.

It is possible to keep the substance for a considerable time in the dark without decomposition taking place. It is easily soluble in alcohol and water, sparingly so in chloroform, and insoluble in ether, light petroleum, or benzene. This diazo-compound is very stable in its behaviour towards reagents and under the action of heat; it is decomposed only on boiling for fifteen minutes with a fairly strong solution of sulphuric acid. It does not explode on heating in a dry tube nor on concussion, and contains no chlorine.

0.1140 gave 0.1684 CO_2 , 0.0590 H_2O , and 0.0180 residue (Na_2SO_4). $\text{C} = 40.28$; $\text{H} = 5.73$; $\text{Na} = 5.11$.

0.1521 gave 9.0 c.c. nitrogen at 18° and 720 mm. $\text{N} = 6.40$.

0.1020 „ 0.0500 BaSO_4 . $\text{S} = 6.66$.

On heating in a dry tube for forty-five minutes at 85° :

0.1123 gave 0.0249 H_2O . $\text{H}_2\text{O} = 22.17$.

$\text{C}_{16}\text{H}_{13}\text{O}_5\text{N}_2\text{SNa}, 6\text{H}_2\text{O}$ requires $\text{C} = 40.28$; $\text{H} = 5.73$; $\text{N} = 5.88$;
 $\text{Na} = 4.83$; $\text{S} = 6.72$; $\text{H}_2\text{O} = 22.60$ per cent.

On adding a solution of platinic chloride to a strong aqueous solution of the substance, a yellow precipitate of the *platinichloride* was obtained, which was separated, washed with water, and dried.

0.1777 gave 0.0370 Pt. $\text{Pt} = 20.82$.

$\text{C}_{32}\text{H}_{26}\text{O}_2\text{N}_4\text{Cl}_6\text{Pt}$ requires $\text{Pt} = 21.50$ per cent.

From moderately strong hydrochloric acid, this salt crystallises with 6 molecules of water.

0.1680 gave 0.0326 Pt. $\text{Pt} = 19.40$.

$\text{C}_{32}\text{H}_{26}\text{O}_2\text{N}_4\text{Cl}_6\text{Pt}, 6\text{H}_2\text{O}$ requires $\text{Pt} = 19.20$ per cent.

On recrystallising the precipitated salt very slowly from dilute hydrochloric acid it absorbs 12 molecules of water.

0.1201 gave 0.0200 Pt. $\text{Pt} = 17.30$.

$\text{C}_{32}\text{H}_{26}\text{O}_2\text{N}_4\text{Cl}_6\text{Pt}, 12\text{H}_2\text{O}$ requires $\text{Pt} = 17.30$ per cent.

The diazo-compound yielded a dark brown precipitate with an alkaline solution of phenol.

On reduction with tin and hydrochloric acid, the diazo-group was eliminated with formation of 2-phenanthryl ethyl ether.

0.0444 gave 0.1408 CO_2 and 0.0269 H_2O . $\text{C} = 86.48$; $\text{H} = 6.73$.

$\text{C}_{16}\text{H}_{14}\text{O}$ requires $\text{C} = 86.47$; $\text{H} = 6.30$ per cent.

3-Ethoxyphenanthraquinonemono-oxime, $\text{OEt} \cdot \text{C}_{14}\text{H}_7 \begin{smallmatrix} \text{O} \\ \llcorner \\ \text{NOH} \end{smallmatrix}$.

Half a gram of 3-ethoxyphenanthraquinone was dissolved in 150 c.c. of absolute alcohol, 0.2 gram of hydroxylamine hydrochloride added, and the mixture heated under a reflux apparatus for two hours on a sand-bath. Part of the alcohol was then evaporated and the residue allowed to stand. On cooling, dark green leaflets of the oxime melting at 174° were obtained. The yield was 0.2 gram.

The filtrate was carefully evaporated to dryness on the water-bath, and after extracting with warm water to remove hydroxylamine, the residue (0.35 gram) was separated and dried.

On crystallising from alcohol, it yielded light yellowish-green leaflets melting at 174° .

The substance is easily soluble in chloroform or methyl alcohol, less

so in ether or ethyl alcohol. The dark green portion is not as soluble in ethyl alcohol as is the light green.

I. Light green portion.

0.1284 gave 6.2 c.c. nitrogen at 20° and 726 mm. $N = 5.27$.

II. Dark green portion.

0.1134 gave 5.6 c.c. nitrogen at 20° and 726 mm. $N = 5.39$.

$C_{16}H_{13}O_3N$ requires $N = 5.24$ per cent.

It is possible that these two substances are stereoisomerides.

2:7-Dibromo-10-nitro-3-phenanthryl Ethyl Ether.

One gram of 10-nitro-3-phenanthryl ethyl ether was heated with 0.45 gram of dry bromine in a sealed tube for four hours at 150—155°. On opening the tube it was found that the substance had become yellowish-green in colour and that the whole of the bromine had disappeared; the yield of the dry crude product was 1 gram. By recrystallisation from petroleum of high boiling point, greenish-yellow needles were obtained (m. p. 203°). The substance dissolves easily in chloroform, not so readily in light petroleum or alcohol, and is insoluble in water.

0.1280 gave 0.0820 AgBr. $Br = 37.20$.

$C_{16}H_{11}O_3NBr_2$ requires $Br = 37.60$ per cent.

The position of the bromine atoms follows from the work of J. Schmidt (*Ber.*, 1904, **37**, 3558, 3568) on dibromophenanthraquinone.

10-Amino-3-phenanthryl Ethyl Ether.

The amino-compound was prepared in exactly the same manner as the corresponding derivative of the 2-series; the reaction in this case, however, was complete in about half an hour.

From 1 gram of the nitro-compound a yield of 0.55 gram was obtained.

On recrystallising from petroleum of high boiling point, a fungus-like mass of very slender, white needles was obtained (m. p. 94°).

0.1656 gave 9.2 c.c. nitrogen at 23° and 722 mm. $N = 5.90$.

$C_{16}H_{15}ON$ requires $N = 5.90$ per cent.

Sodium-3-ethoxy-10-diazophenanthrene Sulphate?

Half a gram of the amino-compound was diazotised as described on p. 1529; but instead of isolating the diazo-compound, the solution was heated for twenty minutes on the water-bath with the object, if

possible, of obtaining the 3-ethoxy-10-phenanthrol. This, however, failed, for after a few minutes' heating a purple, flocculent precipitate was formed, showing that this diazo-compound is not so stable as that of the 2-series. It was afterwards found that this purple precipitate is obtained on rendering the solution alkaline with sodium hydroxide.

Since the attempt to introduce the hydroxyl group in place of the diazo-group proved unsuccessful, another portion of the amino-compound was diazotised and the solution saturated with common salt, when the diazo-compound was precipitated as a pale yellow solid similar to that of the 2-series. On exposure to light for some hours it darkened in colour and finally became brown.

It does not explode on heating in a dry tube or on concussion. It contains sulphur and sodium, but no chlorine.

0.1301 gave 0.2702 CO_2 and 0.0662 H_2O . $\text{C} = 59.00$; $\text{H} = 5.84$.

0.1136 „ 8.4 c.c. nitrogen at 23° and 724 mm. $\text{N} = 7.87$ per cent.

This analysis does not, however, agree with any formula similar to that for the 2-diazo-compound, and the substance was not further investigated.

This research was carried out in the laboratories of the Zürich University during the years 1903 and 1904, and the author desires to express his best thanks to Prof. A. Werner for his kind interest and assistance.

CLII.—*The Velocity of Chemical Change in the Polymethylene Series.*

By NICHOLAS MENSCHUTKIN, sen.

IN this paper an attempt is made to apply to the study of the polymethylene ring compounds the same methods for the determination of the velocity of certain chemical reactions as those which have displayed the regularities in the variation of the velocity with the structure of carbon and heteroatomic open and closed chains.

The inquiry was commenced some years ago, with the substances extracted by W. B. Markownikoff from Caucasian naphtha, but it was abandoned, as only isolated members of the polymethylene series occur in nature. Their systematic study was made possible only by the introduction of synthetical methods for their preparation. Sabatier's method of hydrogenation of aromatic substances was applied in this laboratory by my assistant, S. Gvosdoff, who prepared some

hexamethylene derivatives, but I was only able to finish the work through the kindness of N. D. Zelinsky, Professor at the Moscow University, who sent me several alcohols of the penta-, hexa-, and hepta-methylene series, and I wish to express my warm thanks to Messrs. N. Zelinsky and S. Gvosdoff for their assistance.

1. *Methods employed and their Numerical Results.*

1. *Esterification of Polymethylene Alcohols.*—The velocity of esterification of these alcohols was determined as in my former researches on this subject. An equimolecular mixture of polymethylene alcohol and acetic anhydride, to which was added 15 volumes of benzene, was heated for the necessary time at 100° in small tubes, each containing 4 c.c. of the mixture, quickly cooled in ice-water, and broken in a flask containing water. After twenty-four hours, the acetic acid was titrated with a weak solution of baryta ($N/30$), using phenolphthalein as indicator. Taking *cyclopentanol*, for example, the reaction is shown by the following equation: $C_5H_9 \cdot OH + (C_2H_3O)_2O = C_5H_9 \cdot O \cdot C_2H_3O + C_2H_4O_2$. The esterification constant C is calculated for the bimolecular reaction as follows:

$$C = \frac{x}{A - x} \cdot \frac{1}{t},$$

where $A = 100$, x the extent of change per cent., and t the time in minutes.

Under the above conditions the esterification of the polymethylene alcohols proceeds very regularly. In order to illustrate this, I give one of the series of experiments for the determination of the esterification constant of *cyclopentanol*.

t .	x .	C .
20	27.68	0.0191
40	42.68	0.0186
60	53.20	0.0189
90	62.94	0.0188

Mean..... 0.0189

The esterification constants of other polymethylene alcohols are given in the following table.

Both here and throughout the paper the carbon atom of the polymethylene ring, to which the hydroxyl group is attached, is denoted by (1) and the successive carbon atoms by the numbers 2, 3, 4, &c. This scheme in some cases does not agree with the notation already employed for carbon atoms in polymethylene rings.

The table also contains some details of the characteristic physical properties of the substances employed.

*Pentamethylene Series.*Esterification
constants.

$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \begin{array}{c} 3 \\ 4 \\ 5 \\ 1 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{cycloPentanol(1)}; \text{ b. p. } 140.5^\circ; \\ d_{21/4^\circ} = 0.9395. \end{array} \right\}$	0.0189
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 2\text{-Methylcyclopentanol(1)}; \text{ b. p. } \\ 148-149^\circ; d_{14.5^\circ} = 0.9273. \end{array} \right\}$	0.0126
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{Me} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 3\text{-Methylcyclopentanol(1)}; \text{ b. p. } \\ 151-153^\circ; d_{21/4^\circ} = 0.9122. \end{array} \right\}$	0.0166
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 2:4\text{-Dimethylcyclopentanol(1)}; \\ \text{b. p. } 154-155^\circ; d_{18^\circ} = 0.9083. \end{array} \right\}$	0.0131
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{Me} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 2:5\text{-Dimethylcyclopentanol(1)}; \\ \text{b. p. } 160-161^\circ; d_{18^\circ/4^\circ} = \\ 0.8931; [\alpha]_D + 6.72^\circ. \end{array} \right\}$	0.0085

Hexamethylene Series.

$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \begin{array}{c} 4 \\ 5 \\ 6 \\ 1 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{cycloHexanol(1)}; \text{ b. p. } 160.6^\circ \\ (765.5 \text{ mm.}); d = 0.9471; \text{ from} \\ \text{phenol.} \end{array} \right\}$	0.0138
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \text{CMe} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 1\text{-Methylcyclohexanol(1)}; \text{ m. p. } \\ 26^\circ; \text{ b. p. } 168^\circ (752 \text{ mm.}); \\ d_{23^\circ} = 0.8983. \end{array} \right\}$	0.0004
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 2\text{-Methylcyclohexanol(1)}; \text{ b. p. } \\ 165-166^\circ; d_{17/4^\circ} = 0.9225. \end{array} \right\}$	0.0074
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 3\text{-Methylcyclohexanol(1)}; \text{ b. p. } \\ 91.5-92.5^\circ (35 \text{ mm.}); d_{21/4^\circ} \\ = 0.9137; [\alpha]_D - 3.68^\circ; \text{ from} \\ \text{pulegone.} \end{array} \right\}$	0.0139
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{Me} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 4\text{-Methylcyclohexanol(1)}; \text{ b. p. } \\ 173^\circ; d_0 = 0.9328. \end{array} \right\}$	0.0152
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{array} \text{CMe} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 1:3\text{-Dimethylcyclohexanol(1)}; \\ \text{m. p. } 45-48^\circ; \text{ b. p. } 168^\circ (752 \\ \text{mm.}). \end{array} \right\}$	0.0003
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{cis-3:5-Dimethylcyclohexanol(1)}; \\ \text{b. p. } 185^\circ (760 \text{ mm.}); d_{21^\circ} = \\ 0.9109. \end{array} \right\}$	0.0142
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{trans-3:5-Dimethylcyclohexan-} \\ \text{ol(1)}; \text{ m. p. } 37-38^\circ. \end{array} \right\}$	0.0143
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{cycloHexylcarbinol}; \text{ b. p. } 76^\circ (12 \\ \text{mm.}); d_0 = 0.944. \end{array} \right\}$	0.0250
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CHMe} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{cycloMethylhexylcarbinol}; \text{ b. p. } \\ 81^\circ (15 \text{ mm.}); d_0 = 0.9456. \end{array} \right\}$	0.0071

Heptamethylene Series.

$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \begin{array}{c} 5 \\ 6 \\ 7 \\ 1 \end{array} \text{CH} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} \text{cycloHeptanol(1)}; \text{ b. p. } 184^\circ (742 \\ \text{mm.}); d_{15^\circ} = 0.9595. \end{array} \right\}$	0.0121
$\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CMe} \cdot \text{OH} \dots\dots\dots$	$\left\{ \begin{array}{l} 1\text{-Methylcycloheptanol(1)}; \text{ b. p. } \\ 183-184^\circ. \end{array} \right\}$	0.0003

These esterification constants will be discussed later.

2. *Constant of the Formation of Ethyl cyclohexyl Ether*.—Krafft's reaction was employed; the equation being: $C_6H_5 \cdot SO_2 \cdot OC_2H_5 + C_6H_{11} \cdot OH = C_2H_5 \cdot O \cdot C_6H_{11} + C_6H_5 \cdot SO_2 \cdot OH$. One molecule of the benzenesulphonic ester was mixed with 15 molecules of *cyclohexyl* alcohol. The ordinary solvents cannot be used, as they do not dissolve the sulphonic acid produced by the interaction. The mixture was heated in small sealed tubes to 100° during the number of minutes required, and then the tubes were broken in a flask containing water, the sulphonic acid formed being titrated with baryta water. The reaction proceeds according to the logarithmic law, one of the reacting substances being in large excess:

$$C = \log \frac{A}{A-x} \cdot \frac{1}{t}.$$

The letters have the same signification as in Section 1.

The following series shows the regularity of the reaction and the values obtained for C :

t .	x .	C .
25	9.03	0.00154
44	14.30	0.00152
90	24.07	0.00132
125	29.92	0.00123
Mean.....		0.00140

3. *Constants of the Alkylation of Polymethylene Amines*.—Taking *cyclohexylamine*, for example, the reaction with allyl bromide is represented by the following equation: $2C_6H_{11} \cdot NH_2 + C_3H_5Br = C_6H_{11} \cdot NH \cdot C_3H_5 + C_6H_{11} \cdot NH_2 \cdot HBr$.

The mixture of 2 molecules of amine and 1 molecule of allyl bromide was added to 15 volumes of benzene and heated at 100° in sealed tubes during the time required. The hydrobromide produced was titrated in 95 per cent. alcoholic solution with an alcoholic solution of sodium hydroxide. For the details of this method of estimating the salts of ammonia and the amines, as well as for the determination of constants by this method, the list of papers given on page 1536 may be consulted. The constant is given by the following equation:

$$C = \log \frac{A - x/2}{A - x} \cdot \frac{1}{t}.$$

As an example of the application of this method to the polymethylene amines, I give the numbers obtained in the determination of the alkylation constant of *cyclohexylamine* with allyl bromide.

<i>t.</i>	<i>α.</i>	<i>C.</i>
4	26·31	0·01783
8	44·82	0·01850
12	59·43	0·01988
16	66·25	0·01855
Mean.....		0·01869

The method described was applied to the measurement of the alkylation constants of the following polymethylene amines:

	<i>K.</i>
$\begin{array}{c} \text{CH}_2 \begin{array}{l} \diagup \text{CH}_2 \cdot \text{CH}_2 \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CH} \cdot \text{NH}_2 \dots\dots \dots \end{array}$	$\left\{ \begin{array}{l} \text{cycloHexylamine(1)} ; \text{ b. p. } 133\cdot5- \\ 134^\circ (760 \text{ mm.}) ; d_{20} = 0\cdot8648 ; \\ \text{from aniline.} \end{array} \right\}$
$\begin{array}{c} \text{CH}_2 \begin{array}{l} \diagup \text{CHMe} \cdot \text{CH}_2 \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CH} \cdot \text{NH}_2 \dots\dots \dots \end{array}$	$\left\{ \begin{array}{l} 3\text{-Methylcyclohexylamine(1)} ; \\ \text{b. p. } 145^\circ (752 \text{ mm.}). \end{array} \right\}$
$\begin{array}{c} \text{CH}_2 \begin{array}{l} \diagup \text{CH}_2 \cdot \text{CH}_2 \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}(\text{Pr}^i) \diagup \end{array} \text{CH} \cdot \text{NH}_2 \dots\dots \dots \end{array}$	$\left\{ \begin{array}{l} 5\text{-Methyl-2-}i\text{isopropylcyclohexyl-} \\ \text{amine(1) or } l\text{-menthylamine} ; \\ \text{b. p. } 205^\circ ; d = 0\cdot855 ; [\alpha]_D - 38^\circ. \end{array} \right\}$
$\begin{array}{c} \text{CH}_2 \begin{array}{l} \diagup \text{CHMe} \cdot \text{CH}_2 \diagdown \\ \diagdown \text{CHMe} \cdot \text{CHMe} \diagup \end{array} \text{CH} \cdot \text{NH}_2 \dots\dots \dots \end{array}$	$\left\{ \begin{array}{l} 2 : 3 : 5\text{-Trimethylcyclohexyl-} \\ \text{amine(1)} ; \text{ b. p. } 176-178^\circ (756 \\ \text{mm.}). \end{array} \right\}$
$\begin{array}{c} \text{CHMe} \begin{array}{l} \diagup \text{CH}_2 \cdot \text{CHMe} \diagdown \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \diagup \end{array} \text{CMe} \cdot \text{NH}_2 \dots\dots \dots \end{array}$	$\left\{ \begin{array}{l} 1 : 2 : 4\text{-Trimethylcyclohexyl-} \\ \text{amine(1)} ; \text{ b. p. } 173-174^\circ ; \\ d_{25} / 4^\circ = 0\cdot8292. \end{array} \right\}$

Having described the experimental methods employed in the determination of the velocity of chemical change in the polymethylene series, we may now discuss the constants obtained for the speed of the different reactions. For the sake of simplicity the constants are represented by whole numbers, obtained by multiplication of the results by ten or multiples of ten. In order to compare the properties of the polymethylene cyclic compounds with those of other carbon and heteroatomic chains, the constants obtained by my pupils and myself in the chemical laboratories of the University and the Polytechnikum at St. Petersburg are employed. The sources of these are indicated below.*

II. Formation of Polymethylene Rings.

The closed chains of the polymethylene series and the saturated open chains of normal structure contain the methylene linking $-\text{CH}_2-$, of the same composition and united with the same groups. The comparison of the velocity constants of the same reactions, applied to substances containing the same number of carbon atoms in the chain,

* *Esterification constants.*—N. Menschutkin, *Zeit. physikal. Chem.*, 1887, **1**, 611 ; W. Dabrohotoff, *J. Russ. Phys. Chem. Soc.*, 1895, **27**, 342 ; K. Panoff, *ibid.*, 1903, **35**, 92.

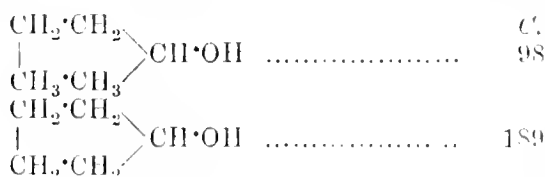
Etherification constants.—W. Zagrebin, *Zeit. physikal. Chem.*, 1900, **34**, 149 ; M. Rosenfeld, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 422.

Alkylation constants.—N. Menschutkin, *Zeit. physikal. Chem.*, 1895, **17**, 193 ; *Ber.*, 1897, **30**, 2780, 2966 ; 1898, **31**, 1424 ; *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 241 ; 1902 **34**, 411 ; N. Nagornoff, *ibid.*, 1897, **29**, 705.

and differing only in the open or closed condition of the chain, will give us data from which we may determine the effect of closing the open chain.

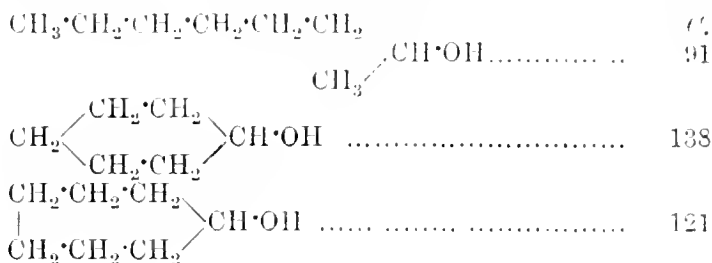
We begin with the comparison of the esterification constants of the secondary polymethylene alcohols, *cyclopentanol*, *cyclohexanol*, and *cycloheptanol*, with those of saturated secondary alcohols containing the group $C_nH_{2n+1}(CH_3)$ of normal structure.

The esterification constants of methylpropylcarbinol and *cyclopentanol* :

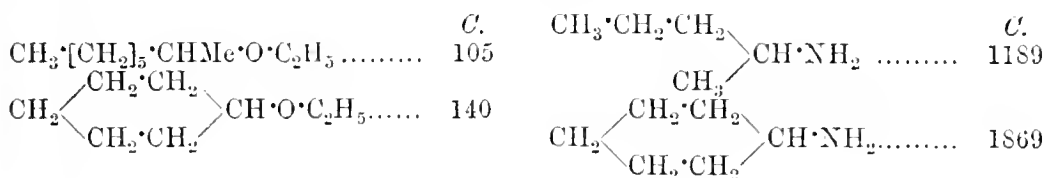


show that the result of closing the open chain, with the loss of two hydrogen atoms and the mutual combination of two carbon atoms, is a great increase in the value of the constant.

The same conclusion is arrived at when the esterification constants of methylhexylcarbinol and *cyclohexanol* or *cycloheptanol* are compared :



An examination of the constants of velocity of other reactions leads to the same result. This is shown by the comparison of (1) the constants of the formation of ethyl *cyclohexyl* ether and of the ether of methylhexylcarbinol and (2) the alkylation constants of *cyclohexylamine* and *n*-amylamine with allyl bromide.



We may conclude, therefore, that *the formation of a polymethylene ring by the closing of the open saturated carbon chain of normal structure proceeds with increase of the constants of velocity.*

The maximum increase of the esterification constants occurs in the case of the formation of the pentamethylene ring; the increase is less in the formation of the hexamethylene ring, and least in that of the heptamethylene ring.

In 1898, when I first compared the alkylation constants of *cyclo*-hexylamine and *n*-amylamine, and pointed out the higher value of the constant of the former, Petrenko-Kritschenko, referring to this fact, remarked that the speed of combination of polymethylene ketones with hydroxylamine is also much higher than in the case of ketones belonging to the open chain series. Since then he has extended his researches to the study of the combination of polymethylene ketones with phenylhydrazine and potassium hydrogen sulphite. This author's numerous experiments (*Ber.*, 1906, **39**, 1452) afford a series of important facts illustrating the increase of speed in the formation of polymethylene rings.

The increase of speed in the formation of a closed chain from an open one is not, however, a property characteristic only of the formation of polymethylene rings, but is a general one for both carbocyclic and heterocyclic systems. As previously stated, the increase of speed of the alkylation of piperidine, which is a heterocyclic compound, is much greater than that of *n*-amylamine, from which piperidine is virtually formed.

	<i>C.</i>
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$	3790
$\text{CH}_2 \begin{array}{c} \diagup \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{NH}$	20,575

In the case of piperidine, the closing of the chain takes place between the nitrogen and carbon atoms, and notwithstanding the fact that in the open chain we are dealing with a primary amine (which gives higher constants), and in the closed chain a secondary amine, the alkylation constant of piperidine is more than five times greater than that of *n*-amylamine.

Does the conclusion arrived at hold only for rings where the atoms are united by single bonds, or will it be applicable also to such rings where the bonds between the atoms are multiple? I am inclined to think that the latter is the case. The existence of such stable alicyclic rings as benzene, the high esterification constants of phenols, the higher constants of aromatic as compared with polymethylene compounds, as described in this paper, is in favour of the application of this rule to alicyclic systems. In the case of heterocyclic systems, we may point to the existence of such absolutely and relatively stable systems as pyridine, thiophen, pyrrole, and others.

In this connection we may consider the formation of closed chain groups in molecules consisting of open chains. The same conditions will apply and the resulting acceleration of speed will be determined by the number of atoms forming the cyclic group. As an example, the facility of the formation of the five-linked lactone ring may be mentioned. Most of the cases of condensation with the formation of

closed chain groups are of a similar nature and there is thus much scope for testing these inductions by experiment.

It is here necessary to explain the chemical meaning of the term "increase of speed." My foregoing investigations on the formation of carbon chains, with respect to the change effected in the constants of speed, show that the speed is greatest in those compounds possessing one carbon atom, and hence containing no chain. The formation of carbon chains is always accompanied by a diminution in the values of the constants, that is, by some loss of speed. In comparing the formation of open and closed chains, however, we find, as shown above, that the formation of closed chains is accompanied by a loss of speed less than is experienced in the case of the formation of open chains, or, in other words, the formation of a closed chain from an open one is accompanied by increase of speed of the chemical change.

III. *Influence of the Number of Carbon Atoms in the Ring on the Esterification Constants of Polymethylene Alcohols.*

In the case of open chain carbon compounds, the formation of homologues is usually effected by the combination of the entering methyl group with the carbon atom of the last link of the chain. Of all alicyclic substances, only the polymethylene, $(\text{CH}_2)_n$, can form such a homologous series, and it is, therefore, necessary to study somewhat extensively the influence of the number of carbon atoms in polymethylene rings on the rate of chemical change.

Three secondary alcohols belonging to the polymethylene series were investigated. Their esterification constants are as follows :

	<i>C.</i>
<i>cyclo</i> Pentanol, $\text{C}_5\text{H}_9\cdot\text{OH}$	189
<i>cyclo</i> Hexanol, $\text{C}_6\text{H}_{11}\cdot\text{OH}$	138
<i>cyclo</i> Heptanol, $\text{C}_7\text{H}_{13}\cdot\text{OH}$	121

It is seen that, by increasing the number of carbon atoms in the ring, the value of the constant diminishes. In order further to investigate the diminution of these constants with increase of molecular weight, we may compare them with the esterification constants of those saturated primary and secondary alcohols in which the homologues are formed by the addition of the $-\text{CH}_2-$ group, as in the polymethylene series. To simplify the figures, all the esterification constants are compared with that of methyl alcohol, which is 0.1118 and is taken as 100. We thus obtain the following numbers :

Normal Primary Alcohols.

	<i>C.</i>
$C_3H_7 \cdot CH_2 \cdot OH$	41.6
$C_4H_9 \cdot CH_2 \cdot OH$	38.4
$C_5H_{11} \cdot CH_2 \cdot OH$	36.8
$C_6H_{13} \cdot CH_2 \cdot OH$	35.1
$C_7H_{15} \cdot CH_2 \cdot OH$	33.7

Secondary Alcohols.

	<i>C.</i>
$CH_3 \cdot CH(CH_3) \cdot OH$	13.2
$C_2H_5 \cdot CH(CH_3) \cdot OH$	11.0
$C_3H_7 \cdot CH(CH_3) \cdot OH$	8.7
$C_6H_{13} \cdot CH(CH_3) \cdot OH$	8.2

Polymethylene Secondary Alcohols.

	<i>C.</i>
<i>cyclo</i> Pentanol, $C_5H_9 \cdot OH$	16.9
<i>cyclo</i> Hexanol, $C_6H_{11} \cdot OH$	12.3
<i>cyclo</i> Heptanol, $C_7H_{13} \cdot OH$	10.8

The tables show that, both in the case of the saturated and polymethylene alcohols, the addition of the group $-CH_2-$ to the open or closed chain gives rise to a decrease in the values of the esterification constants, which is of the same magnitude throughout.

This conclusion is a very important one, and is confirmed by an examination of the esterification constants of the methyl derivatives of the polymethylene alcohols. For this, however, only those alcohols must be compared which contain the side chains in corresponding positions in the ring, as the position of the side chains has a great influence on the value of the constants.

	Esterification constant.	Reduced to the constant of methyl alcohol.
2-Methyl <i>cyclopentanol</i> (1)	126	11.2
2-Methyl <i>cyclohexanol</i> (1)	74	6.6
3-Methyl <i>cyclopentanol</i> (1)	166	14.8
3-Methyl <i>cyclohexanol</i> (1)	139	12.4

The differences in the values of the constants as the molecular weights of the alcohols increase are much the same as those mentioned above.

We come, therefore, to the conclusion that *the rate of decrease of the esterification constants, with the addition to the carbon chain of the group $-CH_2-$, is of the same order in normal saturated alcohols with open chain, as in polymethylene alcohols containing closed chains.*

IV. *The Alcoholic Function of the Polymethylene Secondary Alcohols.*

We have seen that among the homologous polymethylene secondary alcohols, the highest constants are possessed by the derivatives of pentamethylene, then come those of the hexamethylene series; and finally the heptamethylene derivatives have the lowest constants. We may now consider these constants somewhat more fully.

The highest esterification constant of all the polymethylene secondary alcohols belongs to *cyclopentanol*: its constant, 0.0189, is also the highest of all the secondary alcohols investigated. This fact is not in accordance with the rule hitherto observed, that the highest esterification constants are given by saturated secondary alcohols with open chains, and of these by dimethylcarbinol, as the alcohol containing the simplest chain. But the esterification constant of dimethylcarbinol is only 0.0148, and is 25 per cent. less than that of *cyclopentanol*. Amongst the methyl derivatives of *cyclopentanol*, the esterification constant, 0.0166, of 3-methyl*cyclopentanol*(1) is higher than the constant of dimethylcarbinol. The high value of the constants in the pentamethylene series is rendered more evident on comparing these constants with those of the saturated open chain secondary alcohols containing five atoms of carbon. Of these the highest constant is shown by methylpropylcarbinol, but the value is only 0.0098, nearly 50 per cent. lower than that of *cyclopentanol*.

In the hexamethylene series, although the constants are lower than in the pentamethylene series, they are still higher than those of the saturated secondary alcohols containing the same number of carbon atoms. In many cases, the constants of the hexamethylene series are higher than, or very near to, that of dimethylcarbinol: the constant of 4-methyl*cyclohexanol*(1) is 0.0152; *cis*- and *trans*-3:5-dimethyl*cyclohexanol*(1), 0.0143; 3-methyl*cyclohexanol*(1), 0.0139, and *cyclohexanol*(1), the first member of the series, has the esterification constant 0.0138.

The esterification constant of *cycloheptanol* is also higher than those of the alcohols containing seven carbon atoms.

The constants of the above-mentioned polymethylene alcohols are, as has been shown, the highest of all the secondary alcohols studied. This conclusion can be also confirmed by the examination of other constants of chemical change in the hexamethylene series. The constant of the formation of ethyl*cyclohexyl* ether, namely, 0.0140, is higher than in the case of the saturated alcohols containing six carbon atoms. Very important also is the high alkylation constant of *cyclohexylamine*, 0.01869; this constant is the highest among all the amines of the saturated secondary alcohols, the constants of which are very near the value 0.01200, or 30 per cent. lower than that of the cyclic amine.

Thus, all the constants of chemical change point to the conclusion that, under favourable conditions, the constants of the polymethylene series are the highest among those which are known. This conclusion leads us to consider the conditions under which the maximum values for the constants of chemical change were observed. We shall deal principally with the esterification constants, these being more

numerous than the others; the conclusions drawn from these can be applied to the constants of other chemical reactions.

The absolute value of the esterification constant is determined by the following circumstances:

(1) The composition of the alcoholic link of the chain; the primary alcohols giving, under analogous conditions, higher constants than the secondary and tertiary alcohols.

(2) The structure of the chain; the presence of the saturated chain of so-called normal structure, containing no side chains, decreases the values of the constants.

(3) As the formation of every carbon chain proceeds with loss of speed, the maximum constant is possessed by the member containing the simplest chain.

(4) After the present investigation we must add, that under equal conditions the maximum constant is determined by the cyclic structure of the chain.

(5) In view of the very high alkylation constants of the imines of the piperidine series, we must extend the last conclusion and point out that it may be applied to alicyclic and heterocyclic systems, the hydroxy- or the amino-group being combined with the carbon atoms of the ring.

V. *Polymethylene Tertiary Alcohols. Influence of the Side Chains.*

As previously stated, the numbering of the carbon atoms of the polymethylene ring commences with the carbon atom which is combined with the hydroxyl group. The same numbering is given to the side chains: C_1 signifies that the side chain is attached to the same carbon atom of the ring and so forth.

The tertiary polymethylene alcohols are produced when a side chain or group unites with the carbon atom C_1 , which is combined with the hydroxyl group. The esterification of these tertiary alcohols will be principally dealt with.

The first tertiary alcohol investigated was 1-methylcyclohexanol(1) and the series obtained was as follows:

<i>t.</i>	<i>x.</i>	<i>C.</i>
60	2.14	0.00036
121	4.56	0.00041
180	6.98	0.00041
240	9.40	0.00043
Mean.....		0.00040

The esterification of saturated tertiary alcohols led me to expect a very low constant in this case, but as the former alcohols decompose with the production of hydrocarbons, an irregular esterification is obtained.

The polymethylene alcohols, however, are esterified very regularly without decomposition. In order definitely to establish the regular esterification of the polymethylene tertiary alcohols, a special experiment with 1-methylcycloheptanol(1) was made. The experiment lasted ten hours and gave the following very regular numbers:

<i>t.</i>	<i>x.</i>	<i>C.</i>
90	3.54	0.00040
180	5.62	0.00033
360	10.34	0.00032
600	15.94	0.00031

Mean 0.00031

The regular esterification of polymethylene tertiary alcohols shows that in this respect they are analogous to the phenols and tertiary alcohols of the benzene series, but differ from the saturated alcohols.

The esterification being regular, it was possible to determine the esterification constants of the following alcohols:

	<i>C.</i>
1-Methylcyclohexanol(1)	0.0004
1-Methylcycloheptanol(1)	0.0003
1:3-Dimethylcyclohexanol(1)	0.0003

These constants are very low, as are also the constants of other reactions, for example: the alkylation constant of 1:2:4-trimethylcyclohexylamine(1) is 206, and that of saturated tertiary amylamine 270.

We may therefore conclude that: *when the side chain is in the position C₁ of the polymethylene ring a greater decrease in the value of the constant is produced than when it is in any other position in the ring.*

In the open chain series the same effect is produced by the side chain attached to the carbon atom, which is united with the hydroxy- or amino-group. As this fact is already well established, I give only the esterification constants of ethyl, isopropyl, and *tert.*butyl alcohols, and the alkylation constants of ethyl-, isopropyl-, and *tert.*butyl-amines.

	Esterification constant.		Alkylation constant.
CH ₃ ·CH ₂ ·OH	542	CH ₃ ·CH ₂ ·NH ₂	3807
(CH ₃) ₂ CH·OH	148	(CH ₃) ₂ CH·NH ₂	1257
(CH ₃) ₃ C·OH	9	(CH ₃) ₃ C·NH ₂	314

VI. *Ortho- and Diortho-position of the Side Chain.*

The ortho-position of the ring is that where the side chain is combined with the carbon atom (2). Two chains in the ortho-position to the carbon atom (1) are combined with atoms (2) and (5) of the pentamethylene ring, with (2) and (6) of the hexamethylene ring, and with (2) and (7) of the heptamethylene ring.

The side chains here considered are hydrocarbon groups: the chemical nature of the side chain being, as will be seen, of great influence on the effect produced.

In studying the influence of the ortho- and diortho-position of the side chains in the pentamethylene ring, the following derivatives were examined:

	Esterification constants.
<i>cyclo</i> Pentanol(1)	189
2-Methyl <i>cyclopentanol</i> (1) ..	126 (ortho-position of methyl)
2:5-Dimethyl <i>cyclopentanol</i> (1)	85 (diortho-position of ,,)

The side chain in the ortho-position and especially two substituents in the diortho-position decrease the esterification constants of *cyclo*-pentanol to a great extent. The same decrease can be observed if, in 4-methyl*cyclopentanol*(1), we introduce a side chain in the ortho-position.

	C.
4-Methyl <i>cyclopentanol</i> (1)	166
2:4-Dimethyl <i>cyclopentanol</i> (1)	131 (ortho-position)

The hexamethylene ring shows the same behaviour. 2-Methyl-*cyclohexanol*(1) has an esterification constant only half that of *cyclohexanol*(1):

	C.
<i>cyclo</i> Hexanol(1)	138
2-Methyl <i>cyclohexanol</i> (1)...	74 (ortho-position)

* The constants of menthol and *l*-menthylamine are very characteristic, the introduction of the isopropyl group in the ortho-position greatly diminishing the constant.

	Esterification constant.
3-Methyl <i>cyclohexanol</i> (1).....	139
5-Methyl-2-isopropyl <i>cyclohexanol</i> (1)	52 (ortho-position)

	Alkylation constant.
<i>cyclo</i> Hexylamine(1).....	1869
5-Methyl-2-isopropyl <i>cyclohexylamine</i> (1) ...	370 (ortho-position)

The conclusion to be drawn from these facts is that in *polymethylene rings the side chains in the ortho- or diortho-positions greatly diminish the constants of chemical change.*

As will be shown later, this influence of the side chains in the ortho- or diortho-position can be observed in both open and closed chains.

Our knowledge of the influence of the side chains is chiefly derived from the brilliant researches of Victor Meyer in the benzene series. In many cases the decrease of the speed of chemical reaction is so great that many diortho-substitution products have not hitherto been

prepared. I have observed several instances of this decrease in the values of the constants in diortho-compounds of the benzene series. As examples of this may be mentioned the esterification constants of the pairs: phenol—*o*-cresol and *m*-cresol—thymol.

	<i>C.</i>		<i>C.</i>
$\text{C}_6\text{H}_5\cdot\text{OH}$	242	$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH}$	277
$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH}$	72	$\text{CH}_3\cdot\text{C}_6\text{H}_3\cdot\text{OH}$	51
		isoC_3H_7	

The second pair of these phenols shows the relation observed above between 3-methylcyclohexanol(1) and menthol.

We now pass to the consideration of open chains, where the ortho- and diortho-position of the side chains has the same influence. Of many instances observed, mention may be made only of the esterification constants of propyl and isobutyl alcohols and the alkylation constants of propyl-, isobutyl- and *tert.*butyl-amines.

Esterification constant.		Alkylation constant.
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$	480	$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$... 3783
$\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$	401	$\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$... 2759 (ortho-position)
CH_3		CH_3
		CH_3
		$\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$
		CH_3
		791 (diortho- ,,)

The same rule, regarding the influence of the side chains in the ortho-position, holds good also for heteroatomic chains. In the case of open chain compounds, we may cite the constants of formation of ethers and the alkylation constants of secondary amines:

	Etherification constant.
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	816
$\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$	96
CH_3	
CH_3	
	Alkylation constant.
$\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$	2910
$\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$	718
CH_3	
CH_3	

The application of the rule to heterocyclic systems is demonstrated by the alkylation constants of piperidine, α -pipecoline, and *d*-coniine, and by pyridine and α -picoline.

	<i>C.</i>		<i>C.</i>
Piperidine	20575	Pyridine	276
2-Methylpiperidine		2-Methylpyridine	
(α -pipecoline).....	6826 (ortho-position)	(α -picoline)	55
2-isoPropylpiperidine			
(<i>d</i> -coniine)	2684		

We may conclude, therefore, that : *the influence of the side chains in the ortho-position in decreasing the speed of chemical action is a property of all chains whether carbon or heteroatomic, open or closed.*

This rule, however, requires an important modification. Its application is dependent on the chemical nature of the side chains, and the resulting reaction. All the foregoing instances of the application of the rule were obtained with substances containing hydrocarbon groups as side chains, and the chemical reaction consisted in the formation of esters and substituted amines. The exceptions to Victor Meyer's rule are well known, and in my researches I have met with many. In studying the action of dipropylamine on the isomeric bromonitrobenzenes, Nagornoff found that the total displacement of bromine by the dipropylamine group takes place when the nitro-group is in the ortho-position to the bromine atom, whereas there is no action when the nitro-group is in the meta-position. Thus, only by the combined influence of the position of the side chain, its chemical nature, and the ensuing chemical reaction, is the application of the rule assured.

Being applicable to all classes of chains, the rule of the ortho-position of the side chains has no specific importance in the formation of polymethylene closed chains.

VII. *Side Chains in Positions C₃ and C₄ of the Polymethylene Ring.*

The esterification constants of the following hexamethylene alcohols, with the side chains in these positions, were determined :

	C.
<i>cyclo</i> Hexanol(1)	138
3-Methyl <i>cyclo</i> hexanol(1).....	139
4-Methyl <i>cyclo</i> hexanol(1).....	152

On comparing these constants, we see that, where the side chain is farthest from the carbon atom combined with the hydroxyl group, the value of the constant becomes greater, and the constant of 4-methyl-*cyclo*hexanol(1) is even greater than the constant of *cyclo*hexanol(1), the first member of the series. The very great importance of this phenomenon in investigating the nature of closed chains will be more and more evident as we proceed further in the study of this question.

The influence of the combined action of two methyl groups is shown by the esterification constants of the 3 : 5-dimethyl*cyclo*hexanols(1).

	C.
<i>cis</i> -3 : 5-Dimethyl <i>cyclo</i> hexanol(1)	142
<i>trans</i> -3 : 5-Dimethyl <i>cyclo</i> hexanol(1).....	143

The combined action of the methyl groups in both alcohols leads to the constant 143, which is still higher than that of *cyclohexanol*(1).

The case of the dimethylhexanols affords an opportunity of discussing the influence of geometrical isomerism on the esterification constants. The *trans*- and the *cis*-positions of the side chains are identical in their effect on the value of the constants. In this respect, this kind of isomerism is similar to optical isomerism. Panoff studied the esterification of the *d*- and *l*-borneols, and found that the esterification constants in both cases were identical.

In the pentamethylene series it was only possible to experiment with one alcohol containing the side chain in the position C₃. 3-Methylcyclopentanol(1) has the esterification constant 166, which is higher than any in the hexamethylene series, but is lower than that of *cyclopentanol*. It would be expected that the greatest value of the constant in the pentamethylene series would be given by 3:4-dimethylcyclopentanol(1), but this alcohol was not available.

Returning to the question of the increase in the value of the constants when the side chain is in position C₃, it is worthy of note that in open chains no such increase of the constant was observed; the influence of the side chains in the positions C₃ or C₄ was that the value of the constant was less, and never more, than that of the parent substance. I may instance the alkylation constants of *n*-pentylamine and γ -pentylamine:

	C.
CH ₃ ·CH ₂ ·CH ₂ ·CH ₂ ·CH ₂ ·NH ₂	3785
CH ₃ ·CH·CH ₂ ·CH ₂ ·NH ₂ CH ₃	2980

and the esterification constants of *n*-butyl alcohol and *isoamyl* alcohol:

	C.
CH ₃ ·CH ₂ ·CH ₂ ·CH ₂ ·OH	465
CH ₃ ·CH·CH ₂ ·CH ₂ ·OH CH ₃	435

In closed chain compounds, on the other hand, the introduction of the side chain resulted in an increase in the values of the constants. This is illustrated by the following examples.

In the aromatic series may be mentioned the following instances of increase of constants when the side chains are in the position C₃ or C₄ of the benzene ring (C₁ denoting the carbon atom combined with OH or NH₂). We may compare the esterification constants of phenol and *m*-cresol, or the alkylation constants of aniline, *m*-toluidine, and *o*-4-xyldine (see *Ber.*, 1897, 30, 2966; 1898, 31, 1424).

	Esterification constant.		Alkylation constant.
$C_6H_5 \cdot OH$ 1	242	$C_6H_5 \cdot NH_2$ 1	68
$CH_3 \cdot C_6H_4 \cdot OH$ 3 1	277	$CH_3 \cdot C_6H_4 \cdot NH_2$ 3 1	445
		$CH_3 \cdot C_6H_3 \cdot NH_2$ 3 1 CH ₃ 4	707

In all cases the constants increase, the constants of methyl-substituted derivatives being higher than the constants of the first member of the series. The constant of *o*-4-xyldine shows that the increase can extend to more than ten times the value of the constant of the first member of the series.

Passing to heterocyclic systems containing nitrogen, we find the same phenomenon in all cases studied. The alkylation constants of the derivatives of piperidine, pyridine, tetrahydroquinoline, and methyl-(C₃ or C₄)-quinoline are as follows:

	C.		C.
$C_5H_{10} \cdot NH$, piperidine 1	20575	$C_9H_{11}N$, tetrahydroquinoline ... 1	300]
$CH_3 \cdot C_5H_{10} \cdot NH$, 3-methylpiper- 3 1 idine (β -pipercoline) C ₅ H ₉ N, pyridine 1	28109 276	$CH_3 \cdot C_9H_{10}N$, hydro- <i>m</i> -tolu- 3 1 quinoline CH ₃ ·C ₉ H ₁₀ N, hydro- <i>p</i> -toluquin- 4 1 oline C ₉ H ₇ N, quinoline 1	349 610 96
$CH_3 \cdot C_5H_4N$, 3-methylpyridine 3 1 (β -picoline).. ...	445	$CH_3 \cdot C_9H_6N$, γ -methylquinoline* 4 1	159

* The constants in the quinoline series were obtained with methyl bromide, and not allyl bromide, as in the others; in this case, allyl bromide is nearly without action.

Notwithstanding the great difference in the chemical nature of these substances, the different reactions measured, and the enormous differences in the values of the constants (being between 100 and 28,000), in all cases where the side chain is combined with the carbon atom (3) or (4) we observe an increase of the constant.

The conclusion from these facts may be stated as follows: *in all ring systems, alicyclic or heterocyclic, when the substituent methyl groups are in position (3) or (4), an increase in the constant of speed of the reaction is effected.*

This increase of the value of the constants owing to the influence of the side chain is an important property of ring systems, distinguishing them from open chain compounds, and makes it necessary to reconsider what has been said in the second section on the formation of polymethylene rings. If such a ring, having methyl groups in position C₃ or C₄, is formed, it is evident from the above that the decrease of speed in the manner referred to in the second section is less than in any

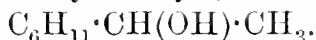
other case. It is difficult to say what circumstances produce such a difference in the act of formation of the ring, the data being insufficient, and especially in the absence of measurements made on compounds with a more complex side chain, such as an ethyl group in place of a methyl group.

In monosubstituted derivatives of those polymethylene rings which contain an even number of carbon atoms, if the side chain is in position C_1 , all the other carbon atoms become identical by pairs in respect to substitution, thus, in the pentamethylene ring, $C_2 = C_5$ and $C_3 = C_4$. In the hexamethylene ring, containing an even number of carbon atoms, $C_2 = C_6$, $C_3 = C_5$, and C_4 has no corresponding carbon atom.

Having in the last three sections described the influence of the side chains combined with C_1 , C_2 , C_3 , C_4 respectively, the most general cases of the said influence in the polymethylene series have been studied.

VIII. *Influence of the Hexamethylene Ring on the Esterification Constants of the Alcohols of the Open Chain Series.*

In the foregoing paragraphs a study was made of the secondary and tertiary polymethylene alcohols in which the alcoholic hydroxyl group was combined with one of the carbon atoms of the ring. We shall now consider the alcohols containing the hydroxyl group in the (open) side chain. In the case where the open side chain has the general formula C_nH_{2n+1} , the introduction of a hydroxyl group may produce primary, secondary, or tertiary alcohols. Of this great division of the polymethylene alcohols, only two representatives belonging to the hexamethylene group were available, namely, primary *cyclohexylcarbinol*, $C_6H_{11} \cdot CH_2 \cdot OH$, and secondary *methylcyclohexylcarbinol*,



Their esterification constants were determined :

	<i>C.</i>
<i>cycloHexylcarbinol</i> , $C_6H_{11} \cdot CH_2 \cdot OH$	250
<i>Methylcyclohexylcarbinol</i> , $C_6H_{11} \cdot CH(OH) \cdot CH_3$...	71

The constants obtained show the usual relation ; the constant of the primary alcohol is much higher than that of the secondary alcohol. The influence of the hexamethylene ring appears in the absolute values of these constants, which may therefore be somewhat more closely examined.

In order to deduce the influence of the hexamethylene ring, we may compare the constant of primary *cyclohexylcarbinol*, namely, 250, with the constants of *n*-heptyl alcohol containing the open chain C_6H_{13} , and with benzyl alcohol containing the benzene ring.

	<i>C.</i>
<i>Methyl alcohol</i> , $CH_3 \cdot OH$	1118
<i>n</i> - <i>Heptyl alcohol</i> , $C_6H_{13} \cdot CH_2 \cdot OH$	393
<i>Benzyl alcohol</i> , $C_6H_5 \cdot CH_2 \cdot OH$	280
<i>cycloHexylcarbinol</i> , $C_6H_{11} \cdot CH_2 \cdot OH$	250

The constant of *cyclohexylcarbinol* is the least, the influence of the hexamethylene ring being not only greater than that exerted by the hexyl group C_6H_{13} , but also than that due to the benzene ring. In order to compare the influence of the hexamethylene ring with the influence of the multiple bonds, no data for the members of the unsaturated series of alcohols with seven carbon atoms are available, and we can therefore only compare the constant of allyl alcohol, $CH_2:CH \cdot CH_2 \cdot OH$, which is 287, with that of propargyl alcohol, $CH:C \cdot CH_2 \cdot OH$, which is 200. These comparisons indicate the position of the polymethylene ring in the scale, showing the influence of the most general classes of carbon chains on the esterification constants of primary alcohols.

The secondary methyl*cyclohexylcarbinol*, $C_6H_{11} \cdot CH(OH) \cdot CH_3$, with its esterification constant 71, gives rise to the same deductions as the foregoing. The saturated methylhexylcarbinol, $C_6H_{13} \cdot CH(OH) \cdot CH_3$, has the constant 91, higher than that of the cyclic alcohol. The constant of the latter alcohol is also much lower in comparison with the constants of secondary polymethylene alcohols, which contain the hydroxyl group combined with the carbon atom of the ring.

IX. *Hexamethylene as a Medium for Chemical Change.*

The study of organic compounds includes the study of their behaviour as solvents. Although non-electrolytes, the so-called indifferent solvents, as my former researches have shown, exert a very great influence on the velocity of the reaction which takes place. Amongst these solvents the hydrocarbons are those which further the activity of chemical reaction to the least degree. Yet between the influence of the hydrocarbons of saturated series and that of the aromatic hydrocarbons the difference is very great, and can be demonstrated by experiment. In order to investigate the behaviour of the polymethylene hydrocarbons as solvents, hexamethylene was chosen. This hydrocarbon was prepared by Gvosdoff by reducing benzene according to Sabatier and Senderens' method; the melting point was $+6.4^\circ$ and the boiling point 81° (760 mm.).

In determining the influence of hexamethylene as a solvent, I studied, as in my former experiments on the subject, the combination of trimethylamine with ethyl iodide to form tetraethylammonium iodide,

$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI.$$

An equimolecular mixture of these substances, diluted with 15 volumes of hexamethylene, was heated at 100° in small sealed tubes. After a certain time the tubes were quickly cooled by ice-water, and, after breaking them in a flask containing water, the ionised iodine was titrated with a solution of silver nitrate. The reaction is dimolecular, and the constant calculated accordingly.

The following table contains the experimental data, showing the velocity of combination of triethylamine with ethyl iodide in hexane, hexamethylene, and benzene :

<i>Hexane.</i>			<i>Hexamethylene.</i>		
<i>t.</i>	<i>x.</i>	<i>C.</i>	<i>t.</i>	<i>x.</i>	<i>C.</i>
60	1.5	0.00018	120	2.27	0.00016
90	2.0	0.00018	180	3.07	0.00017
180	3.6	0.00017	220	3.95	0.00018
Mean.....		0.00018	Mean.....		0.00017

<i>Benzene.</i>		
<i>t.</i>	<i>x.</i>	<i>C.</i>
30	16.75	0.00665
60	27.78	0.00641
90	37.93	0.00672
120	41.91	0.00602
Mean		0.00646

It will be seen from these experiments that hexamethylene gives the same numbers as are obtained with hexane, and both exert a very considerable retarding influence on the reaction as compared with benzene.

X. General Results.

The general results of the study of polymethylene derivatives in respect to the velocity of chemical change may be summed up as follows :

1. The formation of the closed polymethylene ring from an open chain of normal structure proceeds with increase of velocity. The maximum increase occurs in the formation of the pentamethylene ring; in the case of the hexamethylene ring the increase is less, and the heptamethylene ring is formed with the minimum increase of velocity.

2. The increase of velocity at the closing of the open chain is not a specific property of the polymethylene ring, but is a general phenomenon observed in the formation of all ring systems, alicyclic and heterocyclic.

3. The constants of velocity decrease according as the number of methylene groups in the polymethylene rings increases. The decrease is of the same order as is observed in the homologous series of open chain normal saturated carbon compounds.

4. The secondary polymethylene alcohols in which the hydroxyl group is attached to the carbon atom of the ring are typical secondary alcohols. Their esterification constants are higher than those of the

normal saturated secondary alcohols. Hence, the polymethylene alcohols give higher constants than all the secondary alcohols studied. The constants of the derivatives of *cyclopentanol* are the highest; *cyclohexanol* gives much lower values, and *cycloheptanol* still less.

5. The side chain combined with the carbon atom united with the hydroxyl group gives rise to the formation of the polymethylene tertiary alcohols. Their esterification constants are very low, but esterification proceeds regularly; this is not the case with saturated tertiary alcohols, but is characteristic of phenols.

6. When the side chains are in the ortho- and diortho-positions, a great decrease in the esterification constants is observed. This effect, commonly ascribed to the benzene ring alone, is a general property of all classes of chains, whether open or closed, and containing carbon or other elements.

7. When the side chain is in the position (3) or (4) of the polymethylene ring, an increase of the constants is observed, so that in the hexamethylene series the value of the constant of the first member of the series is exceeded.

8. This property is not confined to the polymethylene ring, but applies generally to ringed systems, alicyclic and heterocyclic. As the open chain compounds show no such increase of velocity, this is an important characteristic of closed chains.

9. When a hexamethylene ring is introduced into the open chain of an alcohol, the decrease of the esterification constants is much more than is effected by the benzene ring.

10. Hexamethylene, like hexane, exerts a very considerable retarding influence when used as a solvent in these reactions.

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CLIII.—*Separation of $\alpha\alpha$ - and $\beta\beta$ -Dimethyladipic Acids.*

By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

IN a paper entitled "Synthesis of Dibasic Acids," Blanc (*Bull. Soc. chim.*, 1905,⁴ [iii], 33, 889) states: "Dans les eaux mères de l'acide $\alpha\alpha$ -diméthyladipique, il n'a pas été possible de trouver trace de l'isomère $\beta\beta$. Il n'est cependant pas impossible qu'il en existe parceque le mélange des deux corps est absolument impossible à scinder et ne cristallise pratiquement pas."

In connection with another research (this vol., page 1557), it had

been found that $\alpha\alpha$ -dimethyladipic acid crystallised readily from hydrochloric acid, whereas $\beta\beta$ -dimethyladipic acid did not.

The following rough experiments prove that $\beta\beta$ -dimethyladipic acid is about ten to twelve times as soluble in water saturated with hydrogen chloride as is $\alpha\alpha$ -dimethyladipic acid.

One gram of each acid was dissolved separately in 7 c.c. of water and hydrogen chloride passed into the solution without cooling until no more gas was absorbed. On standing, crystals separated in both cases, but those of the $\beta\beta$ -acid readily redissolved on passing more hydrogen chloride into the solution, whereas those of the $\alpha\alpha$ -acid did not. The solutions were then completely saturated in the cold with hydrogen chloride and allowed to stand fifteen hours, when 0.75 gram of the $\alpha\alpha$ -acid and only 0.05 gram of the $\beta\beta$ -acid separated.

Moreover, $\beta\beta$ -dimethyladipic acid differs appreciably in solubility in water and in a mixture of chloroform and light petroleum (40—60°) from $\alpha\alpha$ -dimethyladipic acid, and it has now been found possible to effect a separation of a mixture of the two acids by taking advantage of these different solubilities.

In the first place, the method was tried with a mixture of one gram each of pure $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids, which was dissolved in 12 c.c. of water and the whole completely saturated in the cold with hydrogen chloride. The containing vessel was a small Erlenmeyer flask, which was corked and allowed to stand until nothing further separated. After filtration, the mother liquor was returned to the flask, the mouth of which was loosely plugged with glass-wool, so as to allow hydrogen chloride gradually to escape, when further crops of crystals were obtained. It is of importance not to allow crystallisation to take place rapidly, otherwise a mixture of the two adipic acids is apt to separate; and therefore, when sufficient hydrogen chloride has escaped, as indicated by the first appearance of solid, the glass-wool plug should be replaced by a cork.

The first fractions always consisted of pure $\alpha\alpha$ -dimethyladipic acid and the process was allowed to continue until a mixture separated, which was easily ascertained, because the melting point of the crystals fell from 86—89° to about 60°. The mother liquor was then evaporated with frequent addition of water, so as to expel all the hydrogen chloride, and it is of great importance that this should be done very thoroughly, otherwise the residue does not solidify readily.

The resulting solid was dissolved in a mixture of chloroform and light petroleum (40—60°), when pure $\beta\beta$ -dimethyladipic acid crystallised out. One such treatment was, however, insufficient to effect a complete separation of the two acids, and on evaporating the chloroform and light petroleum a residue was always obtained, with which the whole separation process was repeated.

The following are the actual details of one of the many experiments tried with one gram of each of $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids dissolved in 12 c.c. of water:

Time of standing.	Amount of fraction.	M. p.	Mixed m. p. with $\alpha\alpha$ -acid.
3 days	0.4 gram	88—89°	88—89°
2 „	0.1 „	88—89	88—89
1 „	0.1 „	87—88	88—89
4 „	0.2 „	87—88	88—89
2 „	0.1 „	80—81	60—61

The mixed melting point of the last fraction of solid with $\beta\beta$ -dimethyladipic acid was 82—83°, and, after one recrystallisation from a mixture of chloroform and light petroleum, 86—87°, showing that it consisted of pure $\beta\beta$ -dimethyladipic acid. The hydrochloric acid solution was then evaporated to dryness, and the residue crystallised from chloroform and light petroleum, when 0.6 gram separated, melting at 85—86°, nor was this melting point altered on mixing with pure $\beta\beta$ -dimethyladipic acid. The whole process was repeated with the solid obtained by evaporating the chloroform and light petroleum mother liquor, giving a further 0.1 gram each of $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acid, so that starting with 1 gram of each acid it was possible to separate from the mixture 0.9 gram of the $\alpha\alpha$ -acid and 0.8 gram of the $\beta\beta$ -acid, both in a pure state.

The method was then further tested by applying it to the mixture of $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids, produced by oxidising the dimethyltetrahydrobenzenes resulting from the action of alcoholic potassium hydroxide on 3-bromo-1:1-dimethylhexahydrobenzene (see page 1556). Seventeen grams of the mixture of hydrocarbons gave 9 grams of solid oxidation product, which were dissolved in six times their weight of water, the solution saturated in the cold with hydrogen chloride, and treated exactly as described above, when the following fractions were obtained:

Amount of fraction.	M. p.	Mixed m. p. with $\alpha\alpha$ -acid.
0.1 gram	86—87°	87—88°
0.4 „	86—87	87—88
0.2 „	88—89	88—89
0.2 „	88—89	88—89
0.6 „	60—62	—

The last fraction was returned to the mother liquor, the whole evaporated, taking care to get rid of all traces of hydrogen chloride, and the residue crystallised from chloroform and light petroleum, when 2.9 grams of solid separated, melting at 84—85°, and when mixed with $\beta\beta$ -dimethyladipic acid at 85—86°. As no further crystallisation took place, the whole was evaporated and the entire process repeated, which gave a further 0.8 gram of pure $\alpha\alpha$ -dimethyladipic acid, 1.0

gram of the $\beta\beta$ -acid, and a residue of 1.3 grams, containing adipic acids as shown by the fluorescein reaction (see below), but which was not further examined. Nine grams of the raw oxidation product gave therefore 1.7 grams of pure $\alpha\alpha$ -dimethyladipic acid, 3.9 grams of pure $\beta\beta$ -dimethyladipic acid, and a residue of 1.3 grams, in all 6.9 grams, indicating a loss of 2.1 grams of material.

In another experiment, 5 grams of solid yielded 1.2 grams of the $\alpha\alpha$ -acid, 2.0 grams of the $\beta\beta$ -acid, and 0.6 gram of a residue, that is, a loss of 1.2 grams. It was ascertained that more than half of this loss took place during the first evaporation of the hydrochloric acid mother liquors, and probably means that there was some volatile oxidation product in the original mixture, otherwise the loss is not large considering the number of crystallisations and filtrations which is necessary.

In the paper by Blanc, already referred to (page 899), it is further stated that " $\beta\beta$ -dimethyladipic acid melts at the same temperature as the $\alpha\alpha$ -acid, namely 87° , and has the same properties, such as crystalline form and solubilities." We cannot agree with any of these statements, for after crystallisation from a mixture of chloroform and light petroleum, $\alpha\alpha$ -dimethyladipic acid melts at 89 — 90° , whereas the $\beta\beta$ -acid, when similarly purified, melts at 86 — 87° . Moreover, the $\alpha\alpha$ -acid separates in radiating clusters of slender needles, whilst the $\beta\beta$ -acid separates in radiating clusters of well-formed, transparent, rhombic plates, which there is no possibility of mistaking; further, the solubilities differ very considerably, as already pointed out (see page 1553).

Another property of these acids which was observed during the course of this work and which is being further investigated, is that they give a very decided fluorescein reaction, and here, again, there is a notable difference in the behaviour of $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids.

To a small quantity of pure $\alpha\alpha$ -dimethyladipic acid, an equal bulk of resorcinol and two or three drops of concentrated sulphuric acid were added, and the whole warmed, when a yellow solution was formed, turning to deep orange-red and, finally, deep reddish-brown. The addition of sodium hydroxide caused the solution to acquire a red-currant colour and a slight green fluorescence, both of which were destroyed by acid; nor did the red-currant colour return on the addition of a large excess of sodium hydroxide, but the solution became yellow, with a very decided green fluorescence.

The colour changes observed when $\beta\beta$ -dimethyladipic acid was heated with resorcinol and sulphuric acid were similar to those described above, but the addition of sodium hydroxide produced a very deep crimson-lake colour, which was much more intense than the

freshly distilled quinoline exactly as previously detailed (Trans., 1906, 89, 45), the only difference being that the reaction temperature was about 195°. The resulting liquid was then passed through the vapour of quinoline, but as this treatment proved insufficient for the complete removal of the bromine, it was boiled with alcoholic potassium hydroxide, the separated hydrocarbon heated for two hours over metallic sodium and distilled, when 13 grams passed over between 114° and 118°. The major portion boiling at 114—116° was analysed:

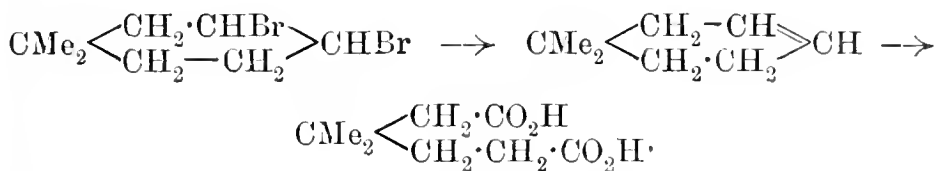
0.1090 gave 0.3523 CO₂ and 0.1172 H₂O. C = 88.15; H = 11.94.

C₈H₁₄ requires C = 87.27; H = 12.73 per cent.

C₈H₁₂ „ C = 88.88; H = 11.11 „

Though the hydrocarbon had the odour and gave the colour reaction characteristic of 1:1-dimethyl-Δ^{2:4}-dihydrobenzene, this analysis proved it to be an undoubted mixture of dimethyldihydro- and dimethyltetrahydro-benzenes.

In order to obtain further evidence on this point, 10 grams of the hydrocarbon were oxidised with potassium permanganate in the usual manner, a process which, though very rapid at first, required ninety-six hours for completion. This fact alone afforded proof of the presence of dimethyltetrahydrobenzene, because this substance is only very slowly attacked by potassium permanganate (compare Trans., 1905, 87, 1502), whereas dimethyldihydrobenzene, is instantly oxidised. Being still under the misapprehension that the dibromo-dimethylhexahydrobenzene, from which the mixture of hydrocarbons had been prepared, was a homogeneous substance, the products expected were *αα*-dimethylsuccinic acid, resulting from the oxidation of the dimethyldihydrobenzene, and *ββ*-dimethyladipic acid, from the oxidation of the dimethyltetrahydrobenzene.



Now it had been ascertained in another series of experiments that *ββ*-dimethyladipic acid does not crystallise at all readily from water saturated with hydrogen chloride, whereas this is the best solvent for the crystallisation of *αα*-dimethylsuccinic acid. The raw oxidation product (6.5 grams) was therefore dissolved in water and the solution saturated with hydrogen chloride, when, on standing, 2.2 grams of needle-shaped crystals separated, melting sharply at 85—86°, and after crystallisation from a mixture of

benzene and light petroleum at 88—89°. On analysis, the following numbers were obtained:

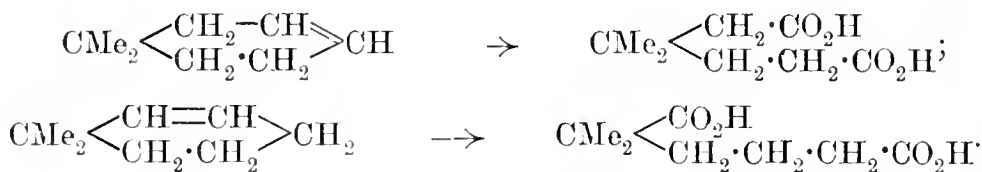
0.1082 gave 0.2190 CO₂ and 0.0804 H₂O. C = 55.20; H = 8.26.
C₈H₁₄O₄ requires C = 55.17; H = 8.04 per cent.

That this substance consisted of *αα*-dimethyladipic acid was proved by the mixed melting point method and by the preparation from it of an anilic acid (compare Blanc, *Bull. Soc. chim.*, 1905, [iii], 33, 894).

The hydrochloric acid mother liquors were then evaporated to dryness, heated with excess of acetyl chloride, and the resulting anhydrides distilled in air, when the majority passed over about 200°; then decomposition set in and an odour of peppermint was evolved, due, no doubt, to the decomposition of some remaining dimethyladipic anhydride. The distillate was shown to consist of the anhydride of *αα*-dimethylsuccinic acid (*a*) by converting a portion into the anilic acid, which crystallised from methyl alcohol in nacreous, scaly needles melting at 185—186° with evolution of gas, and (*b*) by heating the remainder with water, when the acid formed crystallised from hydrochloric acid in needles melting at 140—141°.

This experiment suggested the possibility of being able to separate a mixture of *αα*- and *ββ*-dimethyladipic acids by means of their different solubilities in water saturated with hydrogen chloride, a possibility which has been realised and which is dealt with in a separate communication (see p. 1552).

It also at once proved that the tetrahydrobenzene contained in the mixture of hydrocarbons must have been 1:1-dimethyl-Δ²-tetrahydrobenzene, and therefore that the supposed 1:1-dimethyl-Δ³-tetrahydrobenzene, which formed the starting point of this investigation, was not a homogeneous substance, but consisted of a mixture of 1:1-dimethyl-Δ²-tetrahydrobenzene and 1:1-dimethyl-Δ³-tetrahydrobenzene. If this were so, then on oxidation a mixture of *αα*- and *ββ*-dimethyladipic acids would be obtained, and as it had been found possible, contrary



to the statement of Blanc (*Bull. Soc. chim.*, 1905, [iii], 33, 889), to separate these two acids, a further quantity of 20 grams of dimethyl-tetrahydrobenzene (Trans., 1905, 87, 1499) was prepared and oxidised with potassium permanganate (*ibid.*, p. 1502), when 11.3 grams of solid were obtained. Treated by the method described on p. 1552, this oxidation product yielded 2.9 grams of *αα*-dimethyladipic acid, 4.2 grams of *ββ*-dimethyladipic acid, and 2.1 grams of a residue

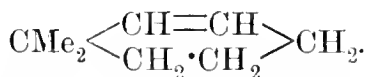
which, in addition to some adipic acids, may have contained acids of lower molecular weight, but which was not further investigated for the reasons given. This proved definitely the correctness of the above inference regarding the composition of the substance previously described as 1:1-dimethyl- Δ^3 -tetrahydrobenzene. Moreover, the liquid never contains equal amounts of the two hydrocarbons, but always a large excess of 1:1-dimethyl- Δ^3 -tetrahydrobenzene.

Many experiments were then made to see if a simple hydrocarbon could be prepared by using diethylaniline or alcoholic potassium hydroxide of different strengths for the removal of the elements of hydrogen bromide from 3-bromo-1:1-dimethylhexahydrobenzene, but in all cases investigation of the oxidation products proved them to consist of $\alpha\alpha$ - and $\beta\beta$ -dimethyladipic acids, although in some instances the mixture contained very small quantities of the $\alpha\alpha$ -acid, which it was impossible to separate by any other means than that described on page 1552. The most favourable conditions for bringing about the latter result were those originally used, thus accounting for the fact that the presence of the $\alpha\alpha$ -acid was then overlooked.

It follows from the above evidence that 3:4-dibromo-1:1-dimethylhexahydrobenzene (III) (Trans., 1905, 87, 1501) is a mixture of this substance with the corresponding 2:3-dibromo-derivative. When treated with quinoline, the former loses the elements of hydrogen bromide to give 1:1-dimethyl- $\Delta^{2:4}$ -dihydrobenzene, which forms the



main portion of the resulting mixture of hydrocarbons. But in the case of 2:3-dibromo-1:1-dimethylhexahydrobenzene, the



removal of the hydrogen bromide cannot take place in an exactly similar manner, because the carbon atom to which the *gem*-dimethyl group is attached has no hydrogen atoms in connection with it. The reaction might take place giving rise to a substance of formula V containing a treble bond, or the two bromine atoms might be alone removed, possibly as a quinoline bromide. The former suggestion does not seem probable, because, although the hydrocarbon would give $\alpha\alpha$ -dimethyladipic acid on oxidation, it would be isomeric with dimethyldihydrobenzene, but analysis showed the substance to be

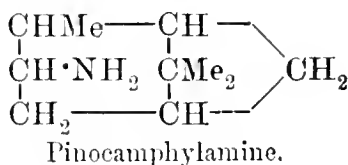
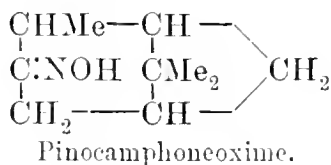
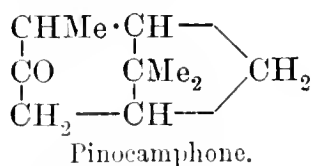
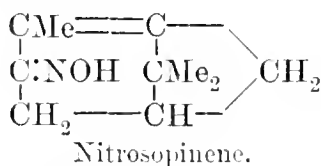
a mixture of dimethyldihydro- and dimethyltetrahydro-benzenes. In the latter case, 1 : 1-dimethyl- Δ^2 -tetrahydrobenzene would result, which would also give *aa*-dimethyladipic acid on oxidation, and, furthermore, its presence would be in agreement with the analytical data.

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CLV.—*The Preparation and Properties of Dihydropinylamine (Pinocamphylamine).*

By WILLIAM AUGUSTUS TILDEN and FREDERICK GEORGE SHEPHEARD, B.Sc.

THE chief product of the reduction of nitrosopinene by the action of zinc and acetic acid is pinylamine which was first obtained by Wallach and Lorentz (*Annalen*, 1892, 268, 197). In addition to pinylamine, however, there is always formed a saturated ketone, pinocamphone, $C_{10}H_{16}O$, isolated for the first time and studied by J. A. Smythe (*Inaug. Diss. Göttingen*, 1898, 16), who obtained a yield corresponding to 22 per cent. of the nitrosopinene employed. The oxime derived from this ketone has been described by Wallach (*Annalen*, 1898, 300, 286) and the product of its reduction by alcohol and sodium is the saturated base dihydropinylamine, or, as it is called by Wallach, pinocamphylamine (*Annalen*, 1900, 313, 367). Assuming G. Wagner's formula for pinene, the following expressions represent the course of these changes and the constitution of pinocamphylamine:



Smythe (*loc. cit.*, 36) attempted the direct reduction of pinylamine by means of amyl alcohol and sodium, but without much success, the amount of the saturated base obtained being too small for complete purification. Wallach contented himself with preparing and analysing the carbamide (m. p. 204°) and the acetyl compound (m. p. 120°).

We find that dihydropinylamine may be prepared easily and in con-

siderable quantity by the direct reduction of nitrosopinene by means of boiling amyl alcohol and sodium, or even by the use of ethyl alcohol and sodium, although in the latter case the yield is much smaller.

Preparation of Dihydropinylamine and its Hydrochloride.—Twenty grams of nitrosopinene were dissolved in boiling amyl alcohol and 24 grams of sodium added in small pieces. After the dissolution of the metal, hydrochloric acid was added in slight excess and the amyl alcohol distilled off in steam. The residue was rendered strongly alkaline with potash, submitted to steam distillation, the distillate extracted with ether, and the base precipitated from the ethereal solution in the form of hydrochloride by passing in gaseous hydrogen chloride. In the most successful experiments, 80 per cent. of the theoretical amount of hydrochloride was obtained.

The hydrochloride is sparingly soluble in water, easily so in alcohol, and crystallises in silky needles which melt and decompose at a temperature above 300° . It sublimes readily and is saturated.

Crystallised from water, the hydrochloride was found to contain two molecules of water of crystallisation. The results of analysis were as follows :

C = 52.98 ; H = 10.95 ; N = 6.54 ; Cl = 15.36 ; H_2O (at 110°) = 16.28.

$C_{10}H_{17}NH_2 \cdot HCl \cdot 2H_2O$ requires C = 53.19 ; H = 10.72 ; N = 6.22 ;

Cl = 15.71 ; and H_2O = 15.95 per cent.

The hydrochloride precipitated from ether and recrystallised from alcohol was anhydrous. It contained Cl = 18.58, whilst $C_{10}H_{17}NH_2 \cdot HCl$ requires Cl = 18.69 per cent.

The free base is a colourless liquid boiling at $198-199^{\circ}$, having an odour very like that of pinylamine.

Platinichloride.—This compound crystallises from alcohol in glistening, orange-yellow plates, insoluble in water and only slightly soluble in cold alcohol or ether.

It contained Pt = 27.02, whilst $(C_{10}H_{17}NH_2)_2H_2PtCl_6$ requires Pt = 27.20 per cent.

Picrate.—This was prepared by dissolving the hydrochloride in warm dilute alcohol, and adding the requisite quantity of picric acid. It crystallises in plates which are moderately soluble in water and melt at 208° .

Analysed, it yielded C = 50.51 and H = 6.36.

$C_{10}H_{17}NH_2 \cdot C_6H_3(NO_2)_3OH$ requires C = 50.10 and H = 6.05 per cent.

Nitrate.—A small quantity of the base was dissolved in acetic acid and a saturated solution of sodium nitrate added. The crystals which were deposited were recrystallised from water, in which the salt is moderately soluble.

The nitrate crystallises in prisms which are easily soluble in alcohol. On being heated it begins to decompose at 176° , and melts with evolution of gas at 180° . It was found to contain $N=12.90$; $C_{10}H_{17}NH_2 \cdot HNO_3$ requiring $N=12.98$ per cent.

Oxalate.—A hot concentrated solution of oxalic acid was added to a dilute alcoholic solution of the base. The salt crystallises in small plates which are only slightly soluble in cold water. It melts at 275° .

Analysed, it gave $N=7.21$, whilst $(C_{10}H_{17}NH_2)_2 \cdot H_2C_2O_4$ requires $N=7.08$ per cent.

Acetyl Derivative.—This was prepared by warming the base with acetic anhydride for about an hour and pouring the product into water. The solid which separated crystallised from petroleum in fine needles which melted at $108-110^{\circ}$, and, although recrystallised several times, could not be obtained with a higher melting point. The melting point of acetyl pinocamphylamine is stated by Wallach to be 120° (*Annalen*, 1900, 313, 368).

Analysis gave $N=7.55$, whilst $C_{10}H_{17} \cdot NH \cdot CO \cdot CH_3$ requires $N=7.19$ per cent.

Benzoyl derivative, prepared by the use of benzoyl chloride and potassium hydroxide, crystallises from alcohol in clusters of needles and melts at 144° .

The benzoyl compound, prepared from the base made from pinocamphone, melts at 144° , and a mixture of the two benzoyl compounds also melts at the same temperature.

Analysis gave $N=5.55$, $C_{10}H_{17} \cdot NH \cdot CO \cdot C_6H_5$ requiring $N=5.46$ per cent.

Carbamide.—The hydrochloride of the base mixed with an aqueous solution of potassium cyanate was warmed on the water-bath until the compound separated out. From dilute alcohol it crystallises in fine needles which melt at 204° , the melting point of the pinocamphyl urea prepared by Wallach.

Analysis gave $N=14.22$, whilst $C_{10}H_{17} \cdot NH \cdot CO \cdot NH_2$ requires $N=14.30$ per cent.

From the comparison of the benzoyl derivative and the carbamides, there can be no doubt about the identity of the base prepared by the direct reduction of nitrosopinene with that obtained through the intermediate steps represented by pinocamphone and its oxime. This is further shown by the production of the alcohol from dihydropinylamine and comparison with pinocampeol obtained by reduction of

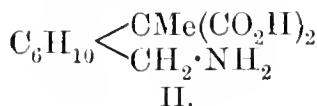
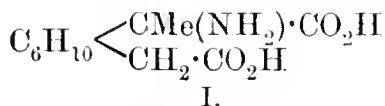
pinocamphone by sodium in the presence of moist ether (Smythe, *loc. cit.*, 21). From dihydropinylamine it was obtained by warming an aqueous solution of the hydrochloride of the base with the calculated quantity of sodium nitrite. The yellow oil which was precipitated was separated by steam distillation, dried, and distilled under reduced pressure. The boiling point at 15 mm. was found to be 103°, that of pinocampheol at the same pressure being, according to Smythe, 104–105°.

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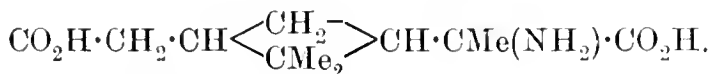
CLVI.—*The Aminodicarboxylic Acid derived from Pinene.*

By WILLIAM AUGUSTUS TILDEN and DONALD FRANCIS BLYTHIER.

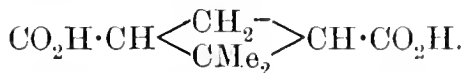
By treating pinene *isonitrosocyanide* with sulphuric acid and hydrolysing the resulting pseudoxime by means of hydrochloric acid, Tilden and Burrows (*Trans.*, 1905, **87**, 344) obtained an amino-acid to which one of the two following formulæ was attributed :



Assuming G. Wagner's formula for pinene (*Ber.*, 1894, **27**, 1651), this compound contains the dimethylated tetramethylene ring to which Baeyer has given the name picean, and formula I must be represented as follows :



The products of the oxidation of this acid should be pinic and ultimately Baeyer's norpic acid (*Ber.*, 1896, **29**, 1910) :



The study of this amino-acid has been again taken up with the object of examining the products of oxidation, but the work is far from complete. The amino-acid hydrochloride when treated with an equivalent quantity of sodium nitrite gave off nitrogen, and the ethereal extract contained a viscid acid substance only sparingly soluble in hot water. The aqueous solution of this acid dissolved lead hydroxide, but the lead and zinc salts could not be made to crystallise. Treated with

a 5 per cent. solution of permanganate, rapid oxidation occurred in the cold. The solution, evaporated to a small bulk, acidified, and extracted with ether, gave a viscid substance possessing a peculiar penetrating odour. These experiments will be renewed with larger quantities. In the meantime the following facts concerning the properties of the amino-acid and of some of its compounds may be recorded.

Preparation of the Hydrochloride.

Pinenecarboxylic acid pseudoxime was dissolved in hydrochloric acid in the proportion of 5 grams to 15 c.c. of concentrated acid and 15 c.c. of water, and the solution heated in sealed tubes to 110—120° for four hours. A small quantity of a dark-coloured liquid floated on the solution, and on steam distillation passed over as a colourless oil which has not been further examined. The acid solution separated from this and evaporated on the steam-bath, gave the hydrochloride, which was purified by recrystallisation from dilute hydrochloric acid. The hydrochloride forms long, colourless prisms or plates which are very soluble in water, and were found to contain 13·07 per cent. of chlorine, whilst the formula $C_{11}H_{19}O_4N, HCl$ requires 13·37 per cent.

It decomposes at about 236° with evolution of carbon dioxide, accompanied by an odour resembling that of cymene.

Preparation of the Acid.

A cold aqueous solution of the hydrochloride, triturated with a slight excess of silver carbonate, yielded a solution from which, on evaporation, after removal of excess of silver by means of hydrogen sulphide, the amino-acid was obtained in crystals.

The acid may also be obtained by mixing a solution of the hydrochloride with a solution of sodium carbonate exactly equivalent to the hydrogen chloride it contains. In consequence of its comparatively slight solubility in water, the acid is soon precipitated in a crystalline state.

It crystallises from water or dilute alcohol in colourless prisms which melt at 273° with evolution of carbon dioxide.

Dried at 100° and analysed, it yielded C = 57·65 ; H = 8·33 ; N = 6·12.

$C_{11}H_{19}O_4N$ requires C = 57·61 ; H = 8·36 ; N = 6·13 per cent.

Nitrate.

The amino-acid dissolves readily in dilute nitric acid, yielding a solution which deposits colourless, radiating needles on evaporation.

The nitrate is very soluble in water, and melts at about 195° with decomposition. It yielded $N = 9.68$, $C_{11}H_{19}O_4N, HNO_3$ requiring $N = 9.61$ per cent.

Acid Oxalate.

This salt is precipitated when concentrated aqueous solutions of the amino-acid hydrochloride and potassium oxalate are mixed. It crystallises from water in long, colourless prisms which contain one molecule of water of crystallisation and which melt at 279° .

On analysis, the oxalate yielded $C = 45.59$; $H = 6.66$; $N = 4.18$; $H_2O = 5.30$.

$C_{11}H_{19}O_4N, H_2C_2O_4, H_2O$ requires $C = 46.26$; $H = 6.87$; $N = 4.16$; $H_2O = 5.34$ per cent.

Copper Salt.

A hot dilute aqueous solution of the amino-acid hydrochloride dissolves copper carbonate with effervescence, forming a bluish-violet solution. If excess of copper carbonate is used, the solution must be filtered rapidly, and, on cooling, the copper salt is deposited in brilliant blue prisms which are practically insoluble in water, alcohol, and ether, but soluble in acetic acid, forming a green solution. When heated, the blue salt becomes violet from partial loss of water of crystallisation. At 150° , the salt loses about $3\frac{1}{2}$ molecules of water, but it cannot be rendered anhydrous without decomposition.

Analysed, it yielded $N = 4.32$, $Cu = 17.46$, and 17.30 .

$C_{11}H_{17}O_4NCu, 4H_2O$ requires $N = 3.87$; $Cu = 17.53$ per cent.

Monoethyl Ester Hydrochloride.

This compound is readily formed when hydrogen chloride gas is passed into a solution of the acid hydrochloride in absolute ethyl alcohol. When nearly saturated, colourless plates are deposited which melt at 241° and contain one molecule of water of crystallisation.

Analysed, the ester yielded $N = 4.97$; $Cl = 11.31$; $H_2O = 5.71$.

$C_{13}H_{23}O_4N, HCl, H_2O$ requires $N = 4.50$; $Cl = 11.37$; $H_2O = 5.78$ per cent.

Monoethyl Ester.

The hydrochloride of the ester dissolves readily in cold water. On adding a cold aqueous solution of the calculated amount of sodium carbonate, the free ester crystallises out after a few minutes. Re-

crystallised from absolute alcohol, it forms slender needles, which retain a molecule of water of crystallisation and melt at 250° .

Analysis gave the following results : $C = 56.04$; $H = 9.00$; $H_2O = 6.59$; $C_{13}H_{23}O_4N, H_2O$ requiring $C = 56.67$; $H = 9.16$; $H_2O = 6.55$ per cent.

Acetyl Derivative of the Acid.

The amino-acid hydrochloride is soluble in a mixture of glacial acetic acid and acetic anhydride, and on heating the solution to a temperature near its boiling point for about five hours acetylation takes place and hydrogen chloride is expelled.

The acetyl compound is deposited on evaporating the solution, and it may be recrystallised from a mixture of glacial acetic acid and ethyl acetate in microscopic, rhombic plates which melt at 223° .

It was found to contain $N = 5.34$, whilst $C_{13}H_{21}O_5N$ requires $N = 5.18$ per cent.

This amino-acid and its hydrochloride appear to interact with benzaldehyde and with glycocine when heated with those substances. The products will be examined when more material has been prepared.

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LONDON, S.W.

CLVII.—*The Description and Spectrographic Analysis of a Meteoric Stone.*

By WALTER NOEL HARTLEY, D.Sc., F.R.S.

THE following are particulars concerning a stony meteorite from Northern Punjab, India. It was sent from the Chemical Laboratory of the Medical College, Lahore, by Lt.-Colonel Donald St. John Dundas Grant, of the India Medical Service, the Chemical Examiner for the Punjab Government.

The label attached was dated 21/7/97, and I received the parcel on September 28th, 1897, at Grantown, Morayshire. Both Col. Grant's letter which preceded the parcel containing the meteorite, and the label enclosed with the stone, described it as having been seen to fall in the Kangra Valley.

This shows it to be of uncommon interest, for of all the meteorites in the fine collection in the British Museum there are but few which have actually been seen in the course of their descent to earth.

Description.—The aërolite measures 3 in. \times 2 in. \times $2\frac{1}{4}$ in. (or 75

mm. \times 51 \times 57); its present weight is 395 grams, and not more than 2 grams, if as much, have been removed.

It was broken on one side before it reached me, and no doubt the fracture may have been caused by its fall. It is of irregular shape, all angularities being rounded by incipient fusion, and the fused surface or skin is for the greater part quite black, but it has a dark red or chocolate-coloured patch on one side. The fractured surface shows a crystalline base with a multitude of irregularly shaped small masses of metallic iron of bright silvery appearance, about 0.5 to 1 mm. in diameter, which are distributed through it. The crystalline stony matter is of a pale grey colour, and judging from the spectrographic analysis it is probably a mixture of calcium orthosilicate with magnesium orthosilicate, corresponding to the minerals enstatite and olivine. On powdering the mass, all the metallic particles were collected by a magnet. On immersion of the meteorite in water in order to take its specific gravity it was found to be porous. The absorbed water was readily removed by suitable desiccation, but the exposed metallic particles on the fractured surface thereby became rusted. Spectrographic analyses were made of the separated metallic and the siliceous portions of the mineral according to the modified method already described (Hartley and Ramage, *Trans.*, 1901, **79**, 61).

The magnetic metallic part was burnt in two portions on ashless filter papers, ten of which in the aggregate showed nothing more than the feeble sodium lines when submitted to the same treatment.

Analysis of the Siliceous Portion.—The reagents used were distilled water, sulphuric acid, ammonium fluoride, ammonium carbonate, and ammonium oxalate. The former left no residue on evaporation. The ammonium fluoride was freshly distilled in a platinum retort, and on subliming 5 grams in a platinum basin it left no trace of any residue. The ammonium carbonate was submitted to the same treatment and was found to be pure. The sulphuric acid in the same manner was also proved to be free from any impurity. The mineral, ground to an impalpable powder in an agate mortar, was decomposed by digesting it with three times its weight of ammonium fluoride mixed with seven times its weight of pure sulphuric acid at about 50° in a platinum basin. When the silicon fluoride had ceased to be evolved, the temperature was raised until all the sulphuric acid and much of the ammonium sulphate had been expelled. The residue from this treatment was boiled with water and a little nitric acid to peroxidise the iron; to this solution, reduced to a small bulk by evaporation, a slight excess of ammonia was added. The precipitate, which contained chiefly alumina and ferric oxide, was collected on an ashless filter paper, dried and ignited in a roll of the same paper in the flame of an oxyhydrogen blow-pipe fitted with platinum jets, and

its spectrum was photographed. The solution containing the heavy metals and metals of the calcium group was mixed first with ammonium carbonate and filtered, then with ammonium oxalate, and again filtered. The filters were dried and burnt, the spectra being photographed as before. The filtrate from the ammonium oxalate precipitate was evaporated to a small volume, absorbed by ashless filter papers, and burnt, another photograph being taken. All these manipulations were carried on in platinum vessels.

The following are the results of the analyses :

The Metallic Portion.—Spectra 1 and 2 yielded iron, nickel, chromium, cobalt, gallium, manganese, copper, silver, lead, calcium, potassium, and sodium.

The principal constituents of the metal are iron, nickel, cobalt, and chromium, with small quantities of copper, silver, lead, and gallium. The manganese, calcium, potassium, and sodium were present in minute proportions.

The Basic Constituents of the Silicates.—Spectra 3, 4, and 5 showed the presence of iron, nickel, chromium, gallium, magnesium oxide bands, calcium oxide bands, strontium oxide, lead, silver, manganese, potassium, and sodium.

The principal constituents of the silicates are calcium oxide and magnesium oxide. The other bases are in minute proportions.

The aërolite was put aside for the purpose of making careful chemical analyses of the metal and of the non-metallic portion, but owing to various considerations, not the least important being the necessity for breaking off a larger portion of the material, it was decided not to injure it any further, but to preserve it as a museum specimen.

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CLVIII.—*Malacone, a Silicate of Zirconium, containing Argon and Helium.*

By EDWARD STANHOPE KITCHIN and WILLIAM GEORGE WINTERSON,
B.Sc. (Lond.).

THE earliest published account of malacone is contained in a paper by Scherer (*Pogg. Ann.*, 1844, 62, 436), who gave a brief description of the crystallography of this mineral, which forms greyish-black crystals resembling porcelain in appearance and of the same hardness as felspar. Scherer found its specific gravity to be 3.913, whilst as a result of four observations we obtained the value 3.908. If the

mineral, however, is finely powdered and heated to remove water, its specific gravity rises to 4.232 (Scherer, 4.2). Of the published analyses, which are few in number, the following may be taken as examples :

	SiO ₂ .	ZrO ₂ .	Fe ₂ O ₃ .	Y ₂ O ₃ .	Mn ₂ O ₃ .	CaO.	MgO.	H ₂ O.
1.	31.31	63.4	0.41	0.34	—	0.39	0.11	3.03
2.	31.87	59.32	3.11	—	1.20	—	—	4.00
3.	31.05	61.44	3.29	—	0.14	0.08	—	3.09

No. 1 is given by Scherer (*loc. cit.*) and refers to a specimen of malacone received from Hitterö ; No. 2 is by Hermann, of a specimen from Ilmougeburg ; and No. 3 is given by Rammelsberg (*Mineralchemie*, p. 891), the mineral analysed having been collected at Chauteloupe, Haute-Vienne.

These analyses all agree fairly well and correspond with the formula (according to Scherer and checked by us)



The percentages calculated from this formula are :

$$\text{SiO}_2 = 32.6 ; \text{ZrO}_2 = 64.22 ; \text{H}_2\text{O} = 3.18.$$

The fact that this mineral was found to be radioactive, and to give off argon when heated, rendered it desirable that a more careful examination should be undertaken.

Its radioactivity is very slight, as the following figures show :

Natural leak of electroscope...	56 mins.
10 mg. powdered malacone ...	$\left\{ \begin{array}{l} a. \quad 46 \text{ ,, } 20 \text{ secs.} \\ b. \quad 46 \text{ ,, } 21 \text{ ,,} \end{array} \right.$
10 mg. standard U ₃ O ₈	4 ,, 0 ,,

These measurements were always made over the same ten divisions of the electroscope scale. By calculating the number of divisions which would have been passed over in 100 mins. (*a*) by the natural leak, (*b*) by the leak induced by malacone, and (*c*) by that from uranium oxide, and then discounting the effect of the natural leak in the two latter cases, it is possible to compare directly the radioactivity of malacone with that of uranium oxide. Thus it is found that taking the radioactivity of uranium oxide equal to 1, that of malacone becomes 0.0161.

Now subsequent analysis showed that malacone contained 0.33 per cent. of uranium, which on the same scale would give malacone a radioactivity of only 0.0033. Hence the difference between the found and calculated values, that is, 0.01636—0.0033 would give the radioactivity due to any constituent other than uranium. This is equal to 0.01306. In other words, of the total radioactivity of the

substance, 20.1 per cent. is due to uranium and 79.9 to other substance or substances.

Further, it was found that all the radioactivity of malacone is obtained after decomposition of the mineral in the zirconium dioxide. Whether this extra activity is due to radium or not it is impossible to say at present. The theory that radium is a decomposition product of uranium has been proposed by several observers, and may prove the explanation of this phenomenon. Experiments are about to be undertaken in order to ascertain if radium is present; these will have to be performed in the ordinary way, by measuring the rate of decay of the emanation and by estimating the "saturation current" by means of the electrometer.

If it can be shown that the uranium actually does disintegrate into radium, then the presence of the argon may be explained as accompanying or being produced during that change, precisely as helium undoubtedly is from radium. This is, however, scarcely likely, as then argon should be found in all the uranium minerals or, at any rate, in all those known to contain radium, but experience shows that this is not the case. The argon was extracted from the mineral and measured as follows. A specimen of the malacone, well crystallised, was powdered and fused in a hard-glass tube with potassium hydrogen sulphate; the gas was collected by the help of a Töpler's pump and analysed. Discounting the sulphur dioxide and oxygen due to the decomposition of the acid sulphate, it consisted of carbon dioxide, hydrogen, nitrogen, argon, and helium; per hundred grams of mineral, the amount of each gas by volume and by weight is given in the following table:

	Volume in c.c.'s at N.T.P.	Weight in grams.
Carbon dioxide	33.24	0.06530
Hydrogen	0.57	0.00005
Nitrogen.....	0.34	0.00042
Argon	2.82	0.00501
Helium	0.94	0.00017
	<hr/> 37.91	<hr/> 0.07098

The remarkable fact about malacone is its evolving argon when decomposed; in this it stands alone. This fact has been demonstrated in three experiments, so that it is beyond doubt.

To explain the presence of these gases, and also to account for the radioactivity of the malacone, a more detailed examination of the mineral was undertaken. In regard to the radioactivity, Strutt, by examining the emanation from malacone, had surmised that it was due to uranium. The presence of uranium, however, is not mentioned in any of the earlier analyses, so that a special search was made for this, which resulted in its discovery.

The procedure was briefly as follows: crystals of the mineral, free from gangue and extraneous matter, were very finely powdered and sifted through the finest cambric so as to produce an absolutely impalpable powder. The water was estimated by heating a weighed quantity in a boat in a stream of dry air for four hours to a temperature sufficient to soften the Jena glass tube. The whole was then cooled in a vacuum and reweighed, and this treatment continued until no further loss of weight ensued. During this process the powder became somewhat lighter in colour, and its specific gravity increased as previously mentioned. The mean of three such experiments gave, as a result, $\text{H}_2\text{O} = 1.84$ per cent.

To determine the silica, zirconia, &c., Scherer's method was followed. A weighed quantity of the air-dried powder was fused with ten times its weight of mixed sodium and potassium carbonates. Less than this proportion does not appear to decompose the malacone thoroughly. The mixture was first melted over a Bunsen flame until the greater part of the effervescence had ceased, and then heated to whiteness for one hour in a muffle furnace. The fused mass was cooled and then extracted with cold water. By this means the sodium and potassium silicates were dissolved, whilst the zirconates were hydrolysed and zirconium hydroxide, $\text{Zr}(\text{OH})_4$, precipitated as a sandy powder. The precipitate, however, still contained some silica and the solution some zirconia. The precipitate was therefore after drying treated with successive quantities of sulphuric acid and hydrogen fluoride and ignited, operations which were repeated until no further loss of weight occurred. This loss of weight was added to the silica obtained. The silica was estimated in the usual way by repeatedly evaporating the filtrate from the fusion solution nearly to dryness with strong hydrochloric acid, and finally treating with water and filtering. The silica and paper were then strongly ignited and weighed, and the silica found in the zirconium hydroxide added as indicated above. The mean of three experiments gave $\text{Si} = 22.53$ per cent.

The zirconium still in the solution was estimated by carefully neutralising and saturating with sulphur dioxide. The weight of the precipitated zirconium hydroxide was added to that of the precipitate obtained from the solution of the fused carbonates and the whole calculated as ZrO_2 . The mean of three experiments gave $\text{Zr} = 67.78$ per cent.

The solution now contained iron, calcium, magnesium, uranium, and traces of yttrium, cerium, &c.; these were all estimated in the usual way, namely, iron as basic acetate, and weighed as Fe_2O_3 ; calcium as oxalate, weighed as CaO ; magnesium as pyrophosphate, weighed as MgO ; and uranium as ammonium uranate, weighed as U_3O_8 . The yttrium, cerium, &c., were not separated, being present in extremely small amount, though both were separately identified.

The mean result of three concordant analyses were:

Fe_2O_3 .	CaO .	MgO .	U_3O_8 .	$\text{Y}_2\text{O}_3, \text{Ce}_2\text{O}_3, \&c.$
4.93	0.41	0.70	0.33	0.09

The complete analysis is therefore:

ZrO_2 .	SiO_2 .	Fe_2O_3 .	MgO .	CaO .	U_3O_8 .	$\text{Y}_2\text{O}_3, \text{Ce}_2\text{O}_3, \&c.$	H_2O .
67.78	22.53	4.93	0.70	0.41	0.33	0.09	1.84 = 98.57

Discarding all constituents as unessential, except the zirconia and the silica, the percentage of these two would be:

$$\text{ZrO}_2, 75.05; \text{SiO}_2, 24.95 = 100.$$

The formula $3\text{ZrO}_2, 2\text{SiO}_2$ requires

$$\text{ZrO}_2, 75.20; \text{SiO}_2, 24.80 = 100$$

and corresponds to that of a basic silicate of zirconium, $\text{Zr}_3\text{Si}_2\text{O}_{10}$.

Some previous work by Mr. Girvan had led to the suspicion that the zirconia was not homogeneous, for on preparing from it the compound ZrOCl_2 the product was not so definite and well crystallised as a substance prepared from undoubted zirconium nitrate. It was accordingly suspected that the radioactivity of the mineral and the presence of argon in it might be accounted for by the presence of some other element as an impurity which adhered to and contaminated the zirconium.

The method used for checking the equivalent of the zirconium was the indirect one of finding the ratio between zirconium and chlorine in the compound ZrOCl_2 , prepared from the mineral, and comparing it with that in a sample of zirconium oxychloride prepared from zirconium nitrate, $\text{Zr}(\text{NO}_3)_4$. This work had been begun by Girvan, who found in samples from malacone $\text{Zr}:\text{Cl} = 1:1.84$, whereas in a specimen prepared from zirconium nitrate the ratio was $1:2.03$.

But on re-examining the matter it was found that the preparation from malacone was difficult to free from uranium, and Girvan's work was repeated in the following manner.

It was first necessary to prepare a quantity of zirconium oxychloride from malacone. This was done by fusing 14 grams of the finely-powdered mineral with 151 grams of fusion mixture, the same as used in previous analyses. The fusion was performed in a platinum dish, heated for four hours to the highest temperature of a muffle furnace. The product was then extracted with cold water and the zirconium hydroxide filtered off. The zirconium still left in solution was separated as above described and added to the precipitate. There were thus obtained 9.27 grams of a sandy powder.

Now, according to Treadwell, zirconium hydroxide, prepared by the hydrolysis of sodium zirconate with cold water, is entirely soluble in hydrochloric acid. This was, however, found not to be the case; by digesting the precipitate for ten days with concentrated hydrochloric acid in a stream of the gas, only 3.13 grams dissolved, and there was afterwards no change in weight. It was hoped from this that some separation had been effected, but this was not so, as all samples of zirconium oxychloride proved identical. The hydrochloric acid solution was accordingly filtered and the zirconium oxychloride crystallised therefrom. The remaining portion of zirconium hydroxide, insoluble in hydrochloric acid, was brought into solution by placing it in boats in a hard glass tube and heating to dull redness in a stream of chlorine gas, which was saturated with the vapour of carbon tetrachloride by passing it through the latter warmed to 30° . After several days of this treatment, the zirconium hydroxide was converted into the volatile zirconium tetrachloride, which condensed on the cooler parts of the tube. This was dissolved in strong hydrochloric acid, when the zirconium oxychloride crystallised out.

At the same time, some standard zirconium oxychloride was made from nitrate of previously ascertained purity by digesting it for several days with pure hydrochloric acid and crystallising. Finally, this was recrystallised three times from alcohol.

The two samples of zirconium oxychloride from malacone, obtained as above, were kept separate throughout, although no difference was ultimately detected between them. The analyses were all made in the same way, by taking an unweighed quantity of substance and determining in it the zirconium and the chlorine and calculating the ratio $\text{Zr} : \text{Cl}$. The zirconium, which must be estimated first, was precipitated by adding ammonium hydroxide to an aqueous solution of the oxychloride, igniting the precipitated hydroxide, and weighing as ZrO_2 . The chlorine was estimated gravimetrically as chloride. In each case as a check, the silver chloride was reduced to metallic silver and weighed.

At first, results closely resembling those of Girvan were obtained. He had found a ratio $1 : 1.843$, and the ratio was now found to be $1 : 1.824$. Hence it would appear that this sample of zirconium oxychloride was identical with that of Girvan. But on recrystallising the salt from alcohol, the ratio was found steadily but slowly to increase, and, on analysing the mother liquors, uranium was found in them in small and constantly decreasing quantities. The results were as follows, each being the mean of four, two from the original acid-soluble portion and two from the insoluble. These two portions never differed by more than 0.02.

Original crop of crystals from hydrochloric acid	1 : 1.824
Recrystallised once from alcohol.....	1 : 1.830
„ twice „ „	1 : 1.841
„ three times „ „	1 : 1.857
„ four „ „	1 : 1.863
„ seven „ „	1 : 1.892
„ ten „ „	1 : 1.993
„ thirteen „ „	1 : 2.031 (?)

In the last case, the quantity of material had shrunk so much as to render the estimation somewhat difficult to carry out. In any case, however, the ratio was certainly not greater than that given.

The ratio, as found from the pure zirconium oxychloride from the nitrate, was as a mean of six experiments :

$$1 : 2.011.$$

Hence it would appear that the identity of the zirconium in malacone is fully established. In the mother liquors from the above crystallisations, uranium was found in small and decreasing quantities. The presence of this substance undoubtedly accounts for the incorrect ratio of zirconium to chlorine hitherto found, although why it should adhere so obstinately to the zirconium is not easy to say. Also the fact that the zirconium hydroxide can be separated into two fractions by treatment with hydrochloric acid is curious, although a parallel to this is to be found in the behaviour of ferric hydroxide. If the radioactivity of malacone is to be explained, as Strutt suggests, by the presence in it of uranium, how, then, can the presence of argon be accounted for? It is hardly likely that argon is a disintegration product of uranium, as then it should be found in pitchblende and the other uranium ores, a phenomenon which is not found to occur. There is just the possibility, however, that argon may form a compound with zirconium, although this does not appear likely, and experiments are about to be undertaken to investigate this point. There is also the possibility that the argon may have been occluded in the mineral during its formation in the same way as were probably the carbon dioxide and hydrogen. It certainly seems probable that during that period of the earth's history the atmosphere would have contained a greater proportion of the "inactive" gases than it does at present.

Since the commencement of the above work, one of us received the information that another argon-containing mineral had been discovered. No references to this were given at the time, and a careful search through the literature has revealed no account of any

such mineral. Therefore it may be said that in this property malacone is unique.

We have to express our thanks to Sir William Ramsay for suggesting this research, and for his constant advice during its progress.

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CLIX.—*The Action of Nitrogen Sulphide on Certain Metallic Chlorides.*

By OLIVER CHARLES MINTY DAVIS.

DEMARÇAY (*Compt. rend.*, 1880, 91, 854) states that nitrogen sulphide forms compounds with some metallic and non-metallic chlorides, but he does not describe the conditions under which the reactions take place, nor does he give the composition or properties of these derivatives. Although it has not been found possible to obtain derivatives in all the cases mentioned by him, yet several definite compounds of nitrogen sulphide with metallic chlorides have been prepared and examined.

It was found that whereas the trichlorides of arsenic, antimony, and iron gave no compounds with nitrogen sulphide, tetrachloride of tin gave a derivative having the formula $\text{SnCl}_4 \cdot 2\text{N}_4\text{S}_4$. In the case of titanium tetrachloride, a derivative having the formula $\text{N}_4\text{S}_4 \cdot \text{Ti}_2\text{Cl}_6$ was obtained, showing that a portion of the nitrogen sulphide first acted as a reducing agent, presumably with formation of a chlorinated derivative which could not be isolated.

With the pentachlorides of antimony and molybdenum, compounds having the formulæ $\text{SbCl}_5 \cdot \text{N}_4\text{S}_4$ and $\text{MoCl}_5 \cdot \text{N}_4\text{S}_4$ were obtained.

Tungsten hexachloride behaves like titanium tetrachloride, being first reduced and yielding a compound with the formula $\text{WCl}_4 \cdot \text{N}_4\text{S}_4$.

These derivatives were obtained by dissolving the chlorides in a large volume of chloroform, which was carefully dried over phosphorus pentoxide before each experiment. To the cooled chloroform solutions was added the nitrogen sulphide dissolved in hot dry chloroform, the resulting compound in each case separating on mixing the two solutions. Owing to the slight solubility of these derivatives, and the fact that they are decomposed by hot solvents, they cannot be purified by recrystallisation. When exposed to the air they are acted on with

varying degrees of rapidity, and are best preserved beneath dry chloroform, when decomposition is less rapid. It was found necessary to make the analyses immediately after preparation of the compounds owing to their instability.

The nitrogen was determined by Dumas' method, sulphur by Carius', and the chlorine by heating with pure lime. When brought in contact with fuming nitric acid these substances are explosively decomposed.

EXPERIMENTAL.

Action of nitrogen sulphide on :

(1) *Tin Tetrachloride.*

The stannic chloride was distilled immediately before the experiment, and dissolved in a large volume of dry chloroform; the solution was cooled and the nitrogen sulphide dissolved in hot chloroform added in successive portions. A scarlet compound separated immediately, and was rapidly filtered off, washed with dry chloroform, and dried for about ten minutes on a porous plate.

On examination, it was found to consist of well-defined, red, homogeneous crystals which were decomposed by hot solvents, and therefore could not be purified by recrystallisation.

When cautiously heated the crystals began to decompose slowly at 165° , but when rapidly heated vigorous decomposition occurred; on exposure to air, decomposition was gradual, but complete in a few weeks. When kept beneath dry chloroform or ether, crystals of nitrogen sulphide were deposited in each case.

Analysis showed that the compound had been formed by the union of one molecule of stannic chloride with two of nitrogen sulphide.

0.2172 gave 32.6 c.c. moist nitrogen at 21° and 760 mm. $N = 17.60$.

0.4816 „ 0.4486 AgCl. $Cl = 22.98$.

0.2695 „ 0.7854 BaSO₄. $S = 40.01$.

$SnCl_4, 2N_4S_4$ requires $N = 17.83$; $Cl = 22.52$; $S = 40.73$ per cent.

(2) *Titanium Tetrachloride.*

This reagent, unlike stannic chloride, does not unite directly with nitrogen sulphide to give an additive compound. When the reaction is allowed to take place in chloroform solution under the conditions described in the preceding case, a brilliant orange-coloured, crystalline substance separates at once from the solvent. Whereas the compound obtained from stannic chloride may be readily dried on a porous plate

without appreciable change, the titanium compound undergoes very rapid decomposition on exposure to the air.

A nitrogen determination showed that the titanium chloride had been reduced before combination with the nitrogen sulphide took place.

0.2065 gave 20.6 c.c. moist nitrogen at 18° and 756 mm. $N = 11.4$.

N_4S_4, Ti_2Cl_6 requires $N = 11.3$ per cent.

(3) *Antimony Pentachloride.*

The reaction takes place under conditions previously described, the resulting compound being precipitated in well-defined, red needles closely resembling those obtained from stannic chloride. The crystals gradually decompose when exposed to the air, and also when preserved under chloroform; rapid decomposition takes place at about 222° .

On analysis, it was found that 1 molecule of each reacting substance had entered into combination.

0.1781 gave 18.00 c.c. moist nitrogen at 14° and 768 mm. $N = 12.00$.

0.5441 ,, 0.8230 AgCl. $Cl = 37.3$.

0.2026 ,, 0.3860 $BaSO_4$. $S = 26.2$.

$N_4S_4, SbCl_5$ requires $N = 11.6$; $Cl = 36.8$ $S = 26.5$ per cent.

(4) *Molybdenum Pentachloride.*

This reacts readily with nitrogen sulphide, forming a dark brown compound, which undergoes decomposition with great rapidity when separated from the solvent used in its preparation, the colour changing to a dark blue.

A nitrogen determination showed the compound to be analogous to that obtained from antimony pentachloride.

0.1540 gave 15.6 c.c. moist nitrogen at 17° and 772 mm. $N = 11.91$.

$N_4S_4, MoCl_5$ requires $N = 12.24$ per cent.

(5) *Tungsten Hexachloride.*

The reaction which takes place in this case somewhat resembles that which occurs with titanium tetrachloride. On adding nitrogen sulphide to the solution of the chloride, a brown, crystalline compound separated out, which underwent rapid decomposition when exposed to the air.

Analysis showed that the chloride had been reduced before combination with nitrogen sulphide took place.

0.1726 gave 17.00 c.c. moist nitrogen at 21° and 758 mm. $N = 11.17$.

0.3674 „ 0.4160 AgCl. $Cl = 27.98$.

0.1500 „ 0.2780 BaSO₄. $S = 25.44$.

N₄S₄W₂OCl₄ requires $N = 10.97$; $Cl = 27.8$; $S = 25.10$ per cent.

UNIVERSITY COLLEGE,

BRISTOL.

CLX.—*The Addition of Alkyl Halides to Alkylated Sugars and Glucosides.*

By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., Carnegie Fellow, and
AGNES MARION MOODIE, M.A., B.Sc., Carnegie Scholar.

TETRAMETHYL glucose, in common with other methylated sugars, is converted into a mixture of the corresponding alkylated glucosides when subjected to the silver oxide and alkyl iodide reaction, and the β -form of the hexoside invariably predominates in the mixture. This reaction differs sharply in its results from the alternative method of obtaining the alkylated glucosides, in which the methylated sugar is condensed with an alcohol by means of small quantities of hydrogen chloride, as in the latter case the α -form of the product is obtained in much larger proportion. It seemed to us desirable to study more fully the mechanism of the silver oxide reaction, as applied in this way to alkylated sugars, and to elucidate if possible the remarkable tendency of the reaction to produce β -stereoisomerides. Tetramethyl glucose was in the first instance selected for experiment on account of its crystalline nature and its ready conversion into tetramethyl β -methylglucoside when it is dissolved in methyl iodide and treated with silver oxide.

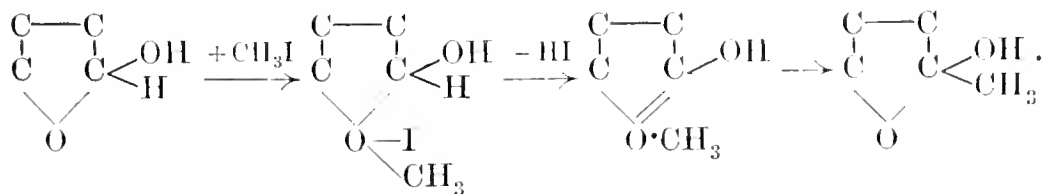
This interaction may proceed in either of two distinct ways. The sugar undoubtedly possesses the γ -oxidic linking, and its unmethylated hydroxyl group is attached to the terminal carbon atom. It seemed possible therefore that, by the action of silver oxide, a silver derivative might be produced in which the metallic atom would occupy the glucosidic position, and that this intermediate compound and methyl iodide would then interact. In the event of the β -form of the sugar reacting in this fashion more readily than the α -isomeride, then the equilibrium mixture of the two forms might ultimately be transformed almost entirely into the alkylated β -glucoside. It was found, however, that no action took place when the equilibrium mixture of tetramethyl glucose was dissolved in pure benzene and shaken with dry silver oxide for several hours. This was carried out at temperatures ranging

from 20° to 50°, conditions which approximate to those which exist during the process of alkylation. The specific rotatory power of the solution remained constant, and the alkylated sugar, when recovered, was found to contain no combined silver and to possess the original melting point. The substitution of acetone and other indifferent solvents for benzene similarly gave negative results.

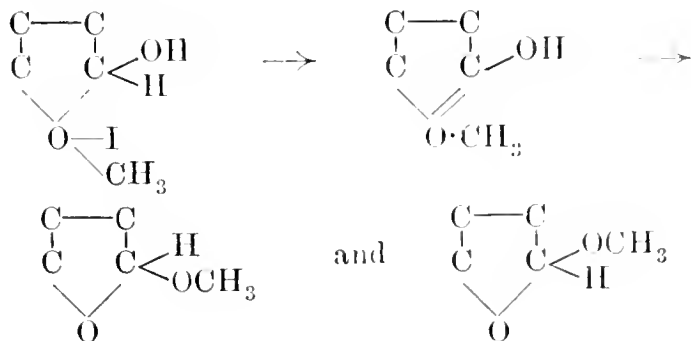
This observation supports the view that the alkyl iodide must play a specific part in the alkylation, either by altering the state of equilibrium of the two forms of the sugar, or by forming an additive compound from which silver oxide would subsequently abstract hydrogen iodide.

The first of these alternatives has been negatived in a previous paper (Trans., 1904, 85, 1070), but the possibility of sugars and glucosides forming additive compounds in which the lactonic oxygen displays quadrivalency has already been pointed out, and E. F. Armstrong (Trans., 1903, 83, 1309) suggests that compounds of this type may play a part in effecting the transformation of the α - and β -forms of a reducing sugar, and in the interconversion of α - and β -glucosides.

The possible addition of methyl iodide to tetramethyl glucose and the subsequent removal of hydrogen iodide may be expressed in the following alternative schemes :



If the action followed the above course, the product would not possess a glucosidic structure, but would consist of a mixture of stereoisomeric methyl hexoses. Moreover, any modification of the above scheme which would account for the formation of a glucoside would be dependent on the transference of the methyl group from the γ -oxidic to the hydroxylic position. As this is most improbable, we conclude that the change can only proceed through the temporary opening of the γ -oxidic ring as shown below :



The change, involving as it does the addition of an alkyl halide and the removal of a different molecule, is not strictly comparable to the tautomeric change $\alpha \rightleftharpoons \beta$ in a reducing sugar, for which Armstrong's theory (*loc. cit.*), on which the first alternative is based, offers a satisfactory explanation.

With the view of testing this hypothesis we examined the rotatory powers of tetramethyl glucose in various alkyl halides, and contrasted the values obtained with those found in ordinary solvents.

The alkylated glucose required was prepared from tetramethyl α -methylglucoside (*loc. cit.*) by boiling an aqueous solution containing 10 per cent. of the alkylated glucoside and 12 per cent. of the hydrogen chloride for thirty minutes. In this way the yield of the crystalline sugar obtained was increased to 87 per cent. of the theoretical amount. The compound was recrystallised several times from light petroleum in order to convert it into the pure α -form. The solutions used for the determinations were uniformly 5 per cent., the concentrations being controlled by means of density determinations. In each case the initial rotatory power was determined as rapidly as possible, after which a trace of alcoholic ammonia was added to promote mutarotation. The permanent values found in the various solvents are contrasted in the following table:

Solvent.	$[\alpha]_D^{20}$.	Solvent.	$[\alpha]_D^{20}$.
Acetone	+89.6°	Methyl iodide	+75.2°
Benzene	88.9	Ethyl iodide	78.3
Carbon tetrachloride...	84.8	Ethyl bromide	78.7
Chloroform.....	84.1	Propyl iodide.....	77.5
Water	83.3	<i>iso</i> Propyl iodide.....	78.6
Alcohol	83.1		

It will be seen that the effect of alkyl halides is invariably to lower the optical rotatory powers considerably, and this was further demonstrated by examination of solutions in benzene and carbon tetrachloride of the sugar, together with 1 molecular proportion of methyl iodide. Even this small quantity of the alkyl halide lowered the specific rotatory powers notably, the values then observed being $[\alpha]_D^{20}$ 83.5° and $[\alpha]_D^{20}$ +81.0° respectively.

It has already been noted (*loc. cit.*) in the case of methyl iodide that this lowering of the rotatory power is not due to the establishment of a different equilibrium in the dissolved sugar, but to a specific effect of the solvent. It is only, however, when the changes undergone by the various solutions during cooling are taken into consideration that evidence is obtained which leads to the conclusion that alkyl iodides form oxonium derivatives with the sugar. For this purpose we utilised the various solutions, already referred to, which had attained the permanent rotatory powers, and determined these at

temperatures ranging from $+40^{\circ}$ to -20° . The conditions of the experiments, which were strictly uniform in every case, may be mentioned here. For temperatures above 0° , a 2-dem. jacketed tube was used, but at lower temperatures a 1-dem. tube, adapted for the use of freezing mixtures and provided with caps containing calcium chloride, was substituted. A thermometer reading to $1/20^{\circ}$ was used throughout, and the concentrations at the different temperatures were controlled by density estimations. Generally each solution was maintained at least one hour at 0° and at -10° before the observations were taken, and in each case, after cooling, the solutions were reheated to 20° and the rotatory powers at this temperature redetermined. Throughout the work precautions were taken to prevent either the access of moisture or evaporation of the solvent.

Our results show that in the case of solutions in acetone, chloroform, or carbon tetrachloride, a continuous and regular increase in specific rotatory power takes place on cooling from $+20^{\circ}$ to -20° , and the same holds true for solutions in benzene within the available range of temperature. Moreover, on reheating the cooled solutions once more to $+20^{\circ}$, the rotatory powers now found for the various intermediate temperatures corresponded with those previously determined for the same temperatures during the cooling process.

Solvent.	$[\alpha]_D^{20}$.	$[\alpha]_D^{10}$.	$[\alpha]_D^5$.	$[\alpha]_D^0$.	$[\alpha]_D^{-10}$.	Behaviour on reheating to 20° .	
Benzene	$+88.9^{\circ}$	$+89.7^{\circ}$	$+90.3^{\circ}$	—	—	Initial $[\alpha]_D$ constant	
Carbon tetrachloride	81.8	87.3	—	$+87.8^{\circ}$	$+89.9^{\circ}$	„	„
Chloroform.....	84.1	85.1	—	86.2	87.2	„	„
Acetone	89.6	92.4	—	96.1	96.9	„	„

On the other hand, it was found that solutions in alkyl halides behaved in a different fashion, as the specific rotatory powers at first increased regularly with fall of temperature, and then suddenly diminished rapidly on further cooling.

The following table contains the results obtained in the case of the solution in ethyl iodide, which serves as a typical example:

Temperature.	20° .	10° .	0° .	-5° .	-10° .
Specific rotatory power	$+78.4^{\circ}$	$+79.7^{\circ}$	$+81.6^{\circ}$	$+83.9^{\circ}$	$+75.3^{\circ}$

This abrupt fall in the values between -5° and -10° is naturally in itself no proof that association of the sugar and solvent had taken place. On reheating the cooled solution from -10° to $+20^{\circ}$, however, the initial specific rotatory power at the latter temperature was $[\alpha]_D^{20} + 81.2^{\circ}$, a value which is higher than that originally found ($+78.4^{\circ}$). On standing, moreover, at constant temperature, distinct mutarotation was observed until practically the original permanent value ($[\alpha]_D^{20} + 78.8^{\circ}$) was attained. As this change proceeded by itself very slowly, but was much hastened by the addition of a trace of

alcoholic ammonia, it seems to be due to the sugar partially undergoing tautomeric change in the sense $\alpha \rightarrow \beta$. The solution on reheating to 20° must therefore have contained excess of the α -isomeride, and this result is accounted for by the assumption that at the low temperature combination between the α -sugar and ethyl iodide had taken place, the removal of the α -form being then followed by a partial transformation of the uncombined portion of the sugar in the direction $\beta \rightarrow \alpha$ in order to restore the equilibrium. The first effect of reheating the solution would be to dissociate the unstable additive compound, and thus liberate the α -sugar. At 20° , the dissociation is practically complete, and the slower tautomeric change of the sugars is then indicated by mutarotation.

According to our explanation of the above results, the complete cycle of optical changes produced on cooling such solutions and then reheating them to the initial temperature should be: (1) a fall in rotatory power due to formation of an oxonium derivative. (2) Upward mutarotation at the low temperature, due to the change $\beta \rightarrow \alpha$ in the uncombined sugar. (3) On reheating, a rapid rise in rotatory power, resulting from the dissociation of the oxonium derivative. (4) Downward mutarotation at the higher temperature, due to the change $\alpha \rightarrow \beta$ in the sugar.

It might be expected that there would be a practical difficulty in observing all these optical effects, as the tautomeric change in the uncombined sugar must proceed simultaneously with the formation or dissociation of the oxonium derivative. As a matter of fact, the latter changes are extremely rapid, whilst the mutarotation of the sugar in alkyl halide solution is comparatively slow. It should thus be possible to observe in succession both series of optical changes. On cooling, the rotatory power of the solution should at first diminish rapidly, and afterwards increase slowly at the same temperature. The converse changes at constant temperature should be observed on heating the solution to a point at which the dissociation of the oxonium derivative takes place.

This cycle of changes was best realised in the case of a solution of tetramethyl glucose in *isopropyl* iodide, as the latter displays the readiest tendency to form an oxonium derivative with the sugar. The solution of the equilibrium mixture of the sugar was rapidly cooled in the polarimeter tube and maintained at 0° . An air thermometer was immersed in the liquid, and readings were taken as soon as the temperature was constant. The initial specific rotatory power observed at 0° was $[\alpha]_D^{0^\circ} + 80.1^\circ$, and this rapidly diminished to $[\alpha]_D^{0^\circ} + 74.1^\circ$. The change due to addition of the iodide was now complete. On adding a trace of alkali, mutarotation occurred, the specific rotatory power increasing to $[\alpha]_D^{0^\circ} + 77.1^\circ$. After standing for eight hours at 0° , the

solution was heated rapidly to 20° and maintained constantly at this temperature. The reverse optical changes were then observed; the rotatory power increased from the initial value, $[\alpha]_D^{20} + 78.4^{\circ}$, to a maximum, $[\alpha]_D^{20} + 80.6^{\circ}$, and afterwards diminished to $[\alpha]_D^{20} + 78.0^{\circ}$.

The complete results for this solution are tabulated below:

Changes in Specific Rotation at Constant Temperature.

Initial $[\alpha]_D^{20}$.		Minimum $[\alpha]_D^{20}$.		Final $[\alpha]_D^{20}$.
+ 80.1°	→	+ 71.1°	→	+ 77.1°
Initial $[\alpha]_D^{20}$.		Maximum $[\alpha]_D^{20}$.		Final $[\alpha]_D^{20}$.
+ 78.4°	→	+ 80.6°	→	+ 78.0°

We have observed a similar series of optical changes at constant temperature in solutions of the sugar in ethyl iodide or *n*-propyl iodide which had been cooled for three hours in a mixture of solid carbon dioxide and ether, and then rapidly heated to 20° and 30° respectively. The observations were:

Solution in Ethyl Iodide.

Initial $[\alpha]_D^{20}$.		Maximum $[\alpha]_D^{20}$.		Final $[\alpha]_D^{20}$.
+ 77.4°	→	+ 79.5°	→	+ 76.8°

Solution in n-Propyl Iodide.

Initial $[\alpha]_D^{30}$.		Maximum $[\alpha]_D^{30}$.		Final $[\alpha]_D^{30}$.
+ 76.8°	→	+ 78.1°	→	+ 76.5°

In view of the above results, we accepted, in our experiments with other alkyl halides, the observation of a sudden diminution of rotatory power on cooling, together with subsequent mutarotation on reheating, as evidence of association of the sugar with the solvent. In addition to alkyl halide solutions, positive results were also obtained in the case of solutions of the sugar in chloroform or carbon tetrachloride containing a molecular proportion of methyl iodide or hydrogen chloride.

Solution in Methyl Iodide.

In this case, owing to the volatility of the solvent, it was found impossible to preserve the concentration of the solution accurately throughout the series of observations, and densities were therefore not taken. The observed rotatory powers are, however, quoted, as, in spite of the contraction of the liquid on cooling, the solution showed the same regularities as other alkyl iodides.

Temperature	20° .	10° .	5° .	0° .	-10° .
Observed rotatory power ...	+ 6.81°	+ 7.36°	+ 7.48°	+ 7.62°	+ 7.95°

Solution in n-Propyl Iodide.

Temperature	40°.	30°.	20°.	10°.	0°.
Specific rotatory power.....	+75·8°	+77·8°	+77·6°	+77·3°	+75·4°

In this case little evidence was given of addition, and the subsequent mutarotation at 20° was slight.

$$[\alpha]_D^{20^\circ} + 77.8^\circ \rightarrow [\alpha]_D^{20^\circ} + 76.2^\circ.$$

Solution in isoPropyl Iodide.

Temperature	30°.	20°.	10°.	0°.	-10°.
Specific rotatory power.....	+77·7°	+78·6°	+79·2°	+72·8°	+70·6°

On reheating to 20°, $[\alpha]_D$ increased rapidly from +73·5° to +78·3° and then diminished slowly to +77°.

Solution in Carbon Tetrachloride containing one Molecular Proportion of Methyl Iodide.

Temperature.....	20°.	0°.	-10°.
Specific rotatory power	+81·0°	+81·2°	+77·0°

Solution in Carbon Tetrachloride containing one per cent. of Hydrogen Chloride.

Temperature	20°.	10°.	5°.	0°.	-5°.	-10°.
Specific rotatory power...	+79·6°	+79·9°	+80·2°	+81·8°	+79·9°	+79·4°

Rotations of α - and β -Modifications of Tetramethyl Methylglucoside in Alkyl Iodides.

Our results show that invariably the α -form of tetramethyl glucose becomes associated with alkyl halides more readily than the β -isomeride. This view was supported by experiments made with the α - and β -modifications of tetramethyl methylglucoside. In the case of glucosides, the problem under consideration is much simplified owing to the absence of ordinary mutarotation. In the cycle of optical changes already described for the case of a reducing sugar, conditions (2) and (3) are thus eliminated, and consequently any alterations in the rotatory power are due either to the formation or dissociation of the oxonium derivatives.

Tetramethyl α -methylglucoside, when cooled in acetone solution, showed practically a constant specific rotatory power. When dissolved in ethyl iodide, the value increased normally during cooling to 0°, but then diminished rapidly on further cooling. As in other cases in

which oxonium formation presumably occurred, heating the cooled solution to 0° had the effect of dissociating the additive compound and an increase of specific rotatory power at the constant temperature of 0° was thus observed. A solution of tetra-acetyl α -methylglucoside in *isopropyl* iodide showed the same regularities, but, on the other hand, tetramethyl β -methylglucoside gave no indication of addition when dissolved in ethyl iodide and similarly treated.

	Solvent.	$[\alpha]_D^{20^{\circ}}$.	$[\alpha]_D^{10^{\circ}}$.	$[\alpha]_D^{0^{\circ}}$.	$[\alpha]_D^{-10^{\circ}}$.
Tetramethyl α -methylglucoside	Acetone	+143.2°	—	+144.6°	+144.6°
" "	Ethyl iodide ...	+138.1	+138.7°	+139.6	+132.9
Tetramethyl β -methylglucoside	Ethyl iodide ...	-17.3	-17.7	-18.6	-18.8
Tetra-acetyl α -methylglucoside	<i>iso</i> Propyl iodide	+127.8	+127.6	+129.0	+126.5

Specific Rotatory Powers of Tetramethyl Mannose at Different Temperatures.

Tetramethyl mannose and tetramethyl α -methylmannoside were found to behave in a similar manner to the corresponding glucose derivatives when dissolved in alkyl iodides, but the optical changes were not so pronounced.

	Solvent.	$[\alpha]_D^{20^{\circ}}$.	$[\alpha]_D^{10^{\circ}}$.	$[\alpha]_D^{0^{\circ}}$.	$[\alpha]_D^{-10^{\circ}}$.	Change in $[\alpha]_D$ on reheating 15° . to 20° .
(1) Tetramethyl mannose	Carbon tetra- chloride	+34.4°	+30.6°	+25.8°	+21.1°	— nil
(2) Tetramethyl mannose	Ethyl iodide..	45.6	43.6	40.9	40.7	— +48.0° +45.7°
(3) Tetramethyl α -methylmannoside	Carbon tetra- chloride	82.3	80.4	77.4	75.3	— nil
(4) Tetramethyl α -methylmannoside	Carbon tetra- chloride + HCl	80.6	78.6	76.0	75.7	+75.8° —

In experiments (2) and (4), the optical effect of association is to counterbalance the regular decrease in rotatory power observed on cooling solutions in non-associating solvents.

Experiments made with non-alkylated sugars or glucosides gave no positive results. Glucose, mannose, α -methylglucoside, and sucrose were selected for experiment, and the specific rotatory powers of each compound determined at the usual temperatures in methyl alcohol containing methyl iodide. The values found were in some cases slightly different from those obtained in pure methyl alcohol, but in no case was a change of rotatory power at constant temperature observed. It would thus appear that the presence of the etheric groups in the alkylated sugar increases the basicity of the γ -oxidic oxygen atom.

Similarly, we find that the specific rotatory power of a typical

hydroxy-ethereal salt such as ethyl tartrate, although much diminished in ethyl iodide, shows no fluctuations corresponding to oxonium formation.

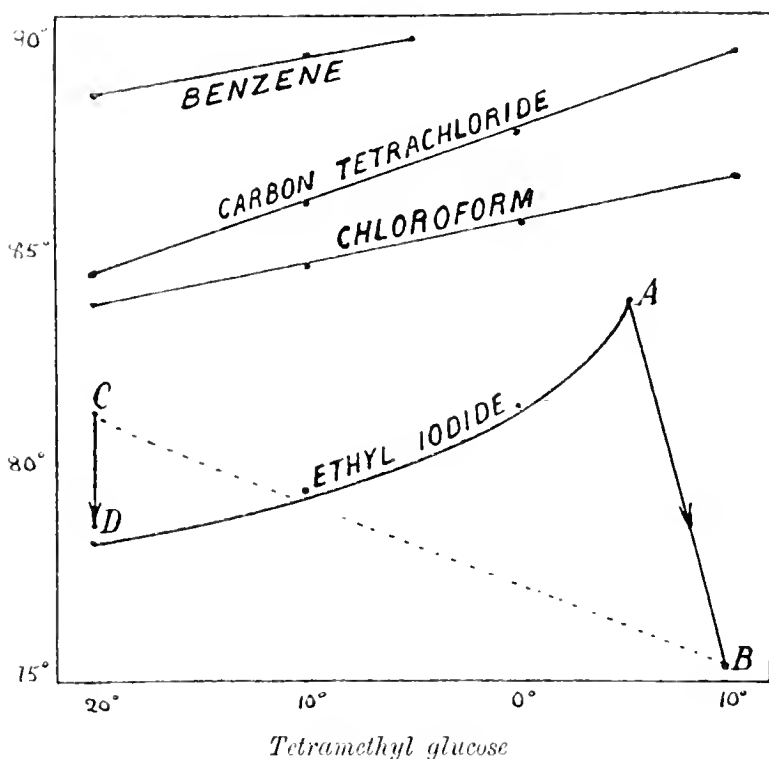
Rotations of Ethyl Tartrate at Different Temperatures.

Solvent.	$[\alpha]_D^{26^\circ}$	$[\alpha]_D^{30^\circ}$	$[\alpha]_D^{20^\circ}$	$[\alpha]_D^{10^\circ}$	$[\alpha]_D^{0^\circ}$	$[\alpha]_D^{-10^\circ}$	$[\alpha]_D^{-20^\circ}$
Carbon tetrachloride...	—	—	+0.98°	-1.1°	-3.4°	-4.7°	—
Ethyl iodide	+0.95°	inactive	-2.21	-4.47	-7.3	-8.8	-10.1°

Our results are best expressed graphically in the form of curves, the abscissæ representing temperatures and the ordinates specific rotatory powers.

In Fig. 1 the behaviour of solutions of tetramethyl glucose in various solvents is contrasted with that of the ethyl iodide solution.

FIG. 1.



The curves for ordinary solvents are seen to be quite normal, but in the case of the alkyl halide the sharp fall *AB* represents oxonium formation between -5° and -10° , whilst *CD* corresponds with the subsequent mutarotation at $+20^\circ$.

Fig. 2 shows the effect of adding one molecular proportion of either methyl iodide or hydrogen chloride to a solution of tetramethyl glucose in carbon tetrachloride. The initial rotatory power is much reduced, and the sharp descent of the curves below 0° indicates the oxonium formation.

In Fig. 3 the curve for the *isopropyl iodide* solution descends steeply from *A* to *B*, indicating that addition begins above 0° . The rapid change *CD* at 20° corresponds with the dissociation of the oxonium derivative.

FIG. 2.

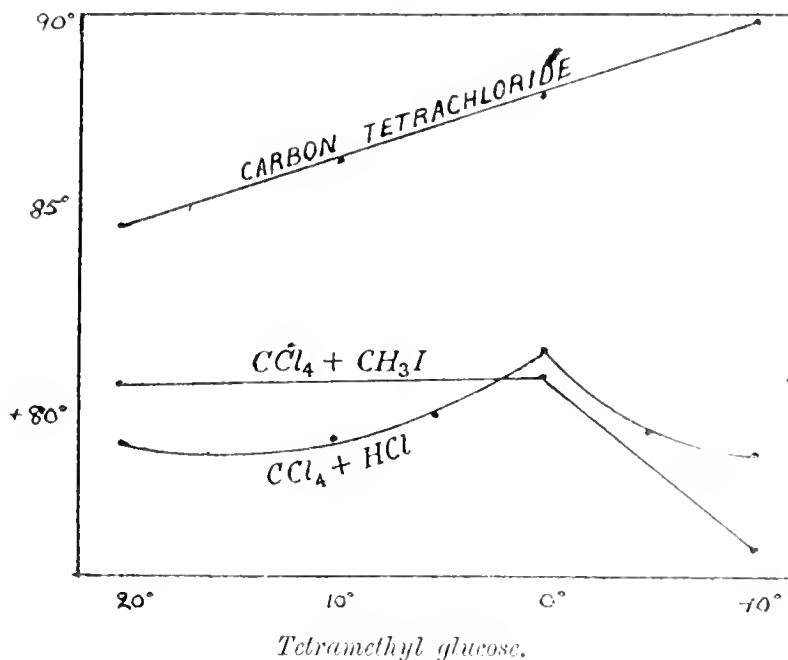
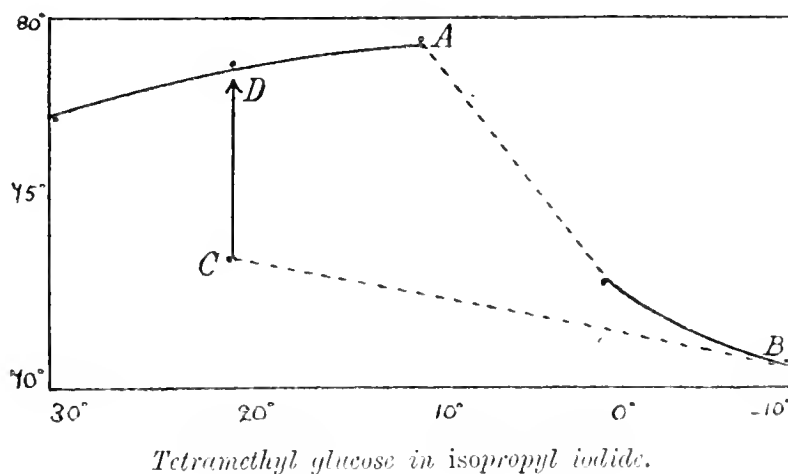


Fig. 4 shows the complete cycle of changes observed with a solution of tetramethyl glucose in *isopropyl iodide*. The rapid fall *AB*

FIG. 3.

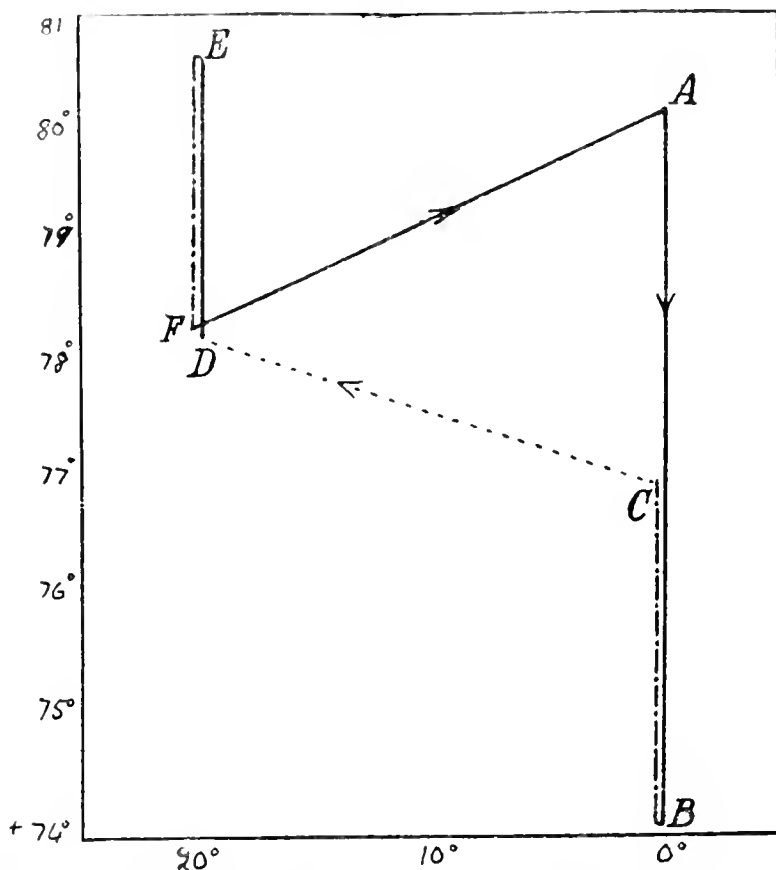


is due to oxonium formation, the subsequent rise *BC* at the same temperature indicates the conversion $\beta \rightarrow \alpha$ in the uncombined sugar, whilst at 20° the rise *DE* and subsequent fall *EF* correspond with the reverse changes.

In Fig. 5 the regular curve for tetramethyl α -methylglucoside in acetone solution is contrasted with the irregular curve obtained for the ethyl iodide solution. The curve for the β -isomeride dissolved in ethyl iodide falls, on the other hand, quite regularly.

There seems to be little doubt that it is the oxygen atom of the γ -oxidic ring which participates in the formation of oxonium compounds from alkylated sugars. Collio and Tickle have pointed out (*Trans.*, 1899, 75, 710) that compounds like dimethylpyrone, in which oxygen

FIG. 4.



Tetramethyl glucose in isopropyl iodide. Changes in specific rotatory power at 0° and +20°.

is linked to a penta-carbon ring, display the readiest tendency to form oxonium derivatives, whilst Bredig (*Zeit. Elektrochem.*, 1896, 3, 116) and Walker (*Ber.*, 1901, 34, 4117) find that ethylene oxide has only slight basic properties. It would thus appear that within certain limits the basicity of the oxygen atom increases with the introduction of more carbon atoms into the ring. Alkylated reducing sugars which possess a γ -oxidic structure, and therefore contain an oxygen atom linked in a tetra-carbon ring, might also be expected to form oxonium compounds. In view of the fact that not only alkylated sugars but

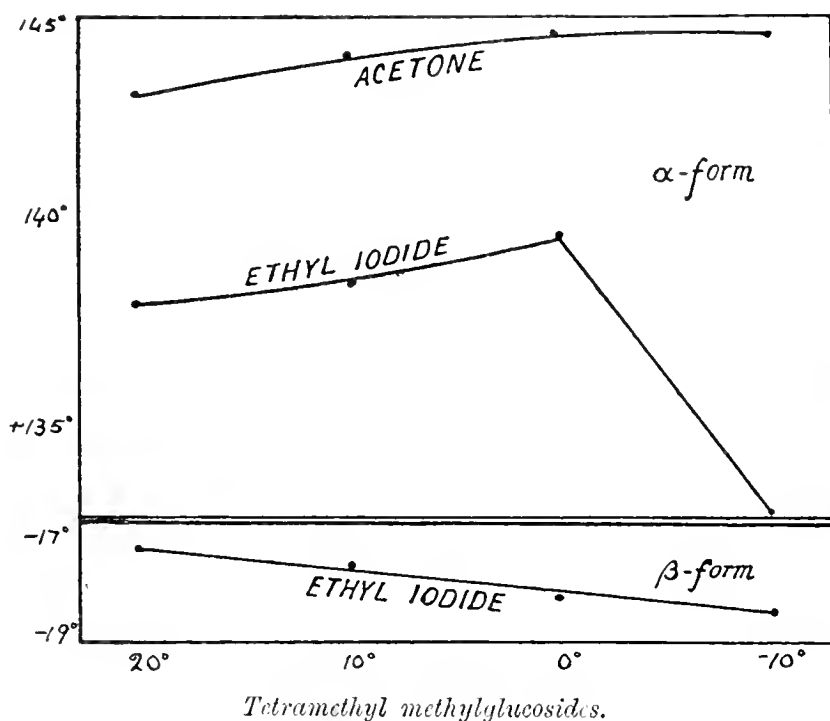
also alkylated glucosides enter into combination with alkyl halides, it is evident that the aldose does not react with these solvents in the aldehydic form, but as a γ -oxide.

It is, moreover, unlikely that any of the etheric oxygen atoms play a part in the addition of the alkyl halides, in view of the fact that the specific rotatory power of ethyl tartrate in ethyl iodide solution, although much lower than in carbon tetrachloride, undergoes a perfectly regular change between $+36^\circ$ and -20° .

Alkylation of Tetramethyl Glucose at Low Temperatures.

In confirmation of our results we have alkylated tetramethyl-glucose with silver oxide and methyl iodide at -10° and find that

FIG. 5.



although the action is slow, the sole product of the change is tetramethyl β -methylglucoside unmixed with the α -isomeride. The materials used were α -tetramethyl glucose (1 mol.), methyl iodide (10 mols.), and dry silver oxide (5 mols.). The sugar was dissolved in the iodide and cooled in a mixture of ice and calcium chloride. The silver oxide was then added in small quantities and the mixture kept actively stirred by a mechanical stirrer, precautions being taken to exclude moisture. After eight hours' treatment, during which the temperature varied from -15° to -10° , the product was extracted with ether. After removal of the solvent, the residue was extracted with light

petroleum, and in this way the product was separated from the sparingly soluble sugar. The extract on evaporation gave an oil which crystallised completely on standing. As the substance melted at 39—41 and behaved like a glucoside towards Fehling's solution, it was evidently tetramethyl β -methylglucoside, which was apparently the only product of the reaction.

Mutarotation of α -Tetramethyl Glucose.

As explained in the introduction, the permanent specific rotatory power of the sugar was determined in several solvents, and, as the material used consisted of the pure α -form, the mutarotation of each solution was observed.

The following table contains the results found in solvents in which the mutarotation of this compound has not hitherto been observed:

Solvent.	Initial $[\alpha]_D^{20}$.	Permanent $[\alpha]_D^{20}$.
Chloroform *	+87.1°	+84.1°
Carbon tetrachloride	92.8	84.9
Benzene	114.5	88.9
Methyl iodide	107.3	75.3
Ethyl iodide	86.7	78.3
Ethyl bromide.....	86.0	78.7

* The specimen of chloroform used contained free acid. This seems to have accelerated the change.

We are extending our work with the view of securing other examples in which oxonium formation may be detected by means of the polarimeter.

Our thanks are due to Professor Purdie for much valuable advice in the interpretation of our results, and also to the Carnegie Trust for a research grant in aid of the work.

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CLXI.—*The Direct Union of Carbon and Hydrogen at High Temperatures.*

By JOHN NORMAN PRING and ROBERT SALMON HUTTON.

Introduction.

PREVIOUS investigations have been limited to a study of the interaction of carbon and hydrogen at temperatures of from 1100—1300°, and to an examination of the compounds produced when an electric arc is maintained between carbon electrodes in hydrogen.

The primary object in view in undertaking the present work was to supplement previous observations by following the course of the reaction at temperatures intermediate between these two extremes.

Unforeseen circumstances, however, have made it necessary to perform a number of experiments at the lower temperatures, the actual limits of the present investigation being from 1000° up to about 2800°.

The early work of Berthelot definitely proved the synthesis of acetylene in the arc, and somewhat later Dewar demonstrated that carbon and hydrogen unite to form acetylene at the temperature of the positive crater of the arc without requiring any of the electrical conditions characteristic of the arc itself.

The important problem of the temperature at which the acetylene first begins to be formed still remained to be investigated.

As to the synthesis of methane at lower temperatures, opinions are somewhat divided. The work of Bone and Jerdan (*Trans.*, 1897, **71**, 41; 1901, **79**, 1042) seemed definitely to have proved the formation of about 1 per cent. of methane at 1200°, but Berthelot, even in his most recent publication on this subject (*Ann. Chim. Phys.*, 1905, [viii], **6**, 183), emphatically expresses his belief that no hydrocarbons are produced at such temperatures, provided the reacting materials are subjected to an exhaustive purification.

The earlier experiments of the present investigation having all shown an unexpectedly small formation of methane, it was deemed advisable to include a study of this second problem.

Experimental Methods.

The chief experimental difficulty lay in the construction of a reaction vessel in which carbon could be heated in contact with hydrogen, the vessel being impervious to gases, and the possibility

of interaction between the carbon and the walls of the vessel being obviated.

These conditions were fulfilled in the apparatus employed, a carbon rod, heated to any desired temperature by the resistance which it offers to an electric current passed through it, being suitably mounted at a considerable distance from the glass or metal walls of the containing vessel.

The carbon rods of 5 and 6 mm. diameter, and about 10 cm. long, were in most cases mounted in water-cooled brass tubes, which served as the terminals for the electric current, by electro-coppering the ends and soldering them into plugs which closed the tubes. In some experiments, however, graphite plugs were fixed to the ends of the water-cooled tubes, and the rods firmly fixed into these plugs, this arrangement being particularly suitable where it is necessary to submit the rods to a preliminary purification by heating in chlorine. In both cases no difficulty is experienced in ensuring good electrical contacts, and arcing is quite avoided, even with high current densities.*

It is surprising how completely the water cooling of the terminals protects the soldered joint from fusing, although practically the whole length of the carbon is at a high and uniform temperature, which in some cases was over 2500°.

Much of the earlier work was carried out in a tubulated glass flask of about 1½ litres capacity, as shown in Fig. 1, a similar egg-shaped glass vessel, provided with a wide tube leading the gas away at the top and admitting it again at the bottom, being also employed in some of the experiments with a view to ensuring a good circulation of the gas, and thus facilitating the attainment of the chemical equilibrium.

These glass vessels work quite satisfactorily, even when the carbon rods are raised to comparatively high temperatures.† As they are capable of standing a vacuum, they proved useful for the preliminary treatment of the rods by heating during evacuation, with a view to expelling occluded and combined hydrogen.

* The following figures give a rough idea of the power expenditure in the experiments with 6 mm. rods; the length of rod used in the different cases varied considerably, so that the figures are of no real value in estimating the temperature, &c.

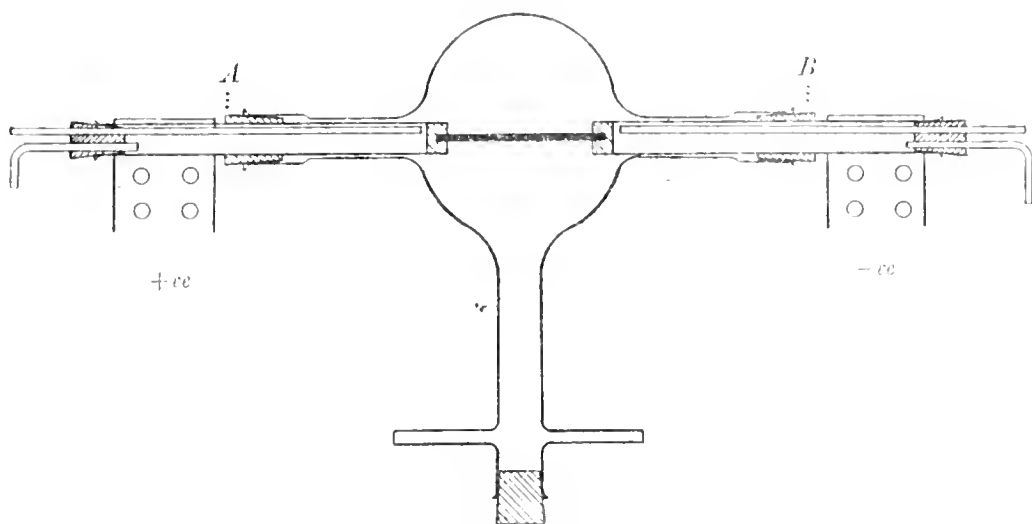
50 amperes at 8 volts at 1000°			
70	„	10	„ 1300
150	„	20	„ 2000
250	„	30	„ 2800

† In the circulation type of apparatus, temperatures up to 2200° were obtained before the glass began to soften; with the simpler type of glass vessel, the highest temperature was about 1900°.

In the later work a water-jacketed metal bell jar, a vertical section of which is shown in Fig. 2, was employed. The bell jar was provided with a mica window, which enabled the rod to be kept in view during the experiment, and was also required for the optical measurement of the temperature. This apparatus proved itself specially valuable for long-continued experiments, and for the higher temperatures, as the walls of the enclosure were kept efficiently cool.

The water-cooled brass tubes were fixed into the reaction vessels by rubber corks, which were coated with cement (marine glue or piccin *).

FIG. 1.



Scale about 1 : 8.

A tubulated glass flask of about 1·5 litres capacity forms the reaction vessel. The carbon rod is soldered into metal plugs, closing the ends of thin brass tubes which form the terminals for the electric current. The brass tubes are water-cooled and are fitted gas-tight at *A* and *B* by means of rubber corks or cement into the long side tubes of the flask.

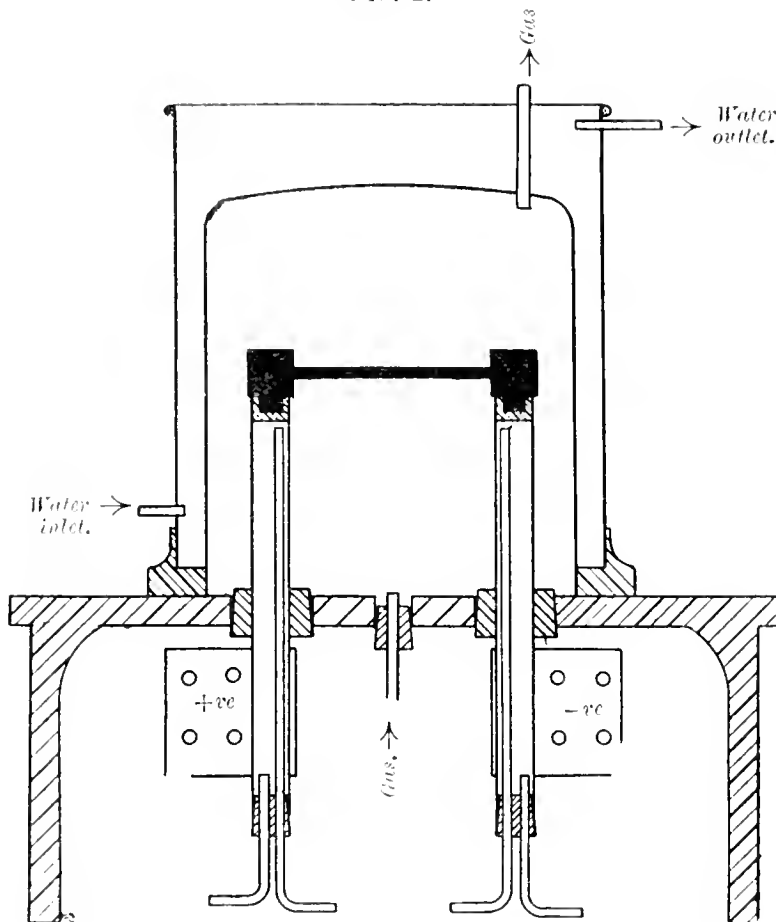
With regard to the purification of the reacting materials, great care was taken in all cases to obtain the hydrogen in a pure state, free from traces of hydrocarbon; for this purpose, electrolytic zinc and pure dilute sulphuric acid were employed, the gases being passed through warm alkaline permanganate, then over a considerable length of red-hot copper gauze, and subsequently dried with calcium chloride, sodium hydroxide, and phosphorus pentoxide.

* (B. Walter, *Ann. Physik*, 1905, [iv], **18**, 860).—Since the cement was in all cases in close proximity to a water-cooled surface, there is little danger of it contaminating the gases by emitting vapours. To test this point, several experiments were carried out, in which pure hydrogen was confined for some hours in a vessel containing some of the cement kept in a water-bath at various temperatures from 15° to 31°. On analysis, the hydrogen was found only to contain from 0·04 to 0·12 per cent. of hydrocarbon, estimated as methane.

The purification of the carbons will be considered in the succeeding section; suffice it to say that in the earlier experiments great reliance was placed on heating the carbon rods in a vacuum before the actual experiment, as also on the continued use of the same carbon rod throughout a long series of experiments.

In carrying out an experiment, the reaction vessel was filled with

FIG. 2.



Scale about 1 : 6.

The reaction vessel consists of a water-jacketed metal bell jar of about 7.5 litres capacity, mounted on an iron table, through which project the water-cooled brass tubes which serve as terminals. The carbon rod is held in graphite end-pieces, which are soldered into metal plugs closing the brass tubes.

pure hydrogen by prolonged displacement, assisted, when possible, by intermittent partial evacuations.

The carbon rod was then brought as rapidly as possible to the desired temperature, which was measured by an optical pyrometer sighted on to the incandescent rod.

After some time the current of hydrogen was stopped, and the

actual experimental run commenced. At intervals, samples (about 50 c.c.) of the gas were drawn from the apparatus by a mercury pipette, and were temporarily stored over glycerol to await the analysis, which was nearly always carried out within a few hours. To replace these small fractions of gas, fresh hydrogen was simultaneously admitted, a slight positive pressure being maintained within the reaction vessel.

After each experiment the hydrogen was displaced for several hours, the heating of the rod being often continued during a portion of this period.

Gas Analysis.

The apparatus employed for the analysis of the gases was of the type designed by Sodeau (*J. Soc. Chem. Ind.*, 1903, 22, 187; see also Noble, *Phil. Trans.*, 1906, A, 205, 204). For this work, the measuring tube with a bulb and narrowed stem was used, the stem being calibrated between 35 and 50 c.c., and the readings being taken to 0.01 c.c. by means of a cathetometer.

Carbon monoxide was determined by absorption with ammoniacal cuprous chloride; the directions for its preparation, given by Hempel, being closely adhered to, since it was necessary to remove this gas completely on account of the subsequent estimation of methane. The cuprous chloride was frequently renewed, and with quite fresh reagents two separate treatments were always performed, and when either of the pipettes had previously been used a third absorption was carried out. Before measuring the total absorption of carbon monoxide, the gas was washed with dilute sulphuric acid.

Methane was estimated by explosion of the residual mixture of gases with oxygen, and subsequent absorption of the carbonic acid with potassium hydroxide. The mixture with oxygen took place in the explosion vessel, on which the volumes were roughly marked. The oxygen, which was generated from "oxylith" in a Kipp's apparatus, was added in a sufficient quantity (about 75 c.c.) to leave from 45 to 50 c.c. of residue after the explosion, which was effected under reduced pressure. A small quantity of dilute acid was then introduced into the explosion pipette, and after this the volume of the remaining gas and its contraction on treatment with potassium hydroxide were carefully measured.

Since the gases always contained a small percentage of nitrogen, and consequently could produce small amounts of nitric oxide on explosion, a number of estimations were carried out with pure hydrogen under otherwise identical conditions. The following values are typical of the results in these experiments:

	Contraction with potassium hydroxide.
(1).....	0.12 per cent.
(2).....	0.11 „
(3).....	0.11 „
(4).....	0.10 „
Mean	0.11 „

This percentage has consequently been subtracted in all the estimations of methane given throughout the paper.

Acetylene was determined by absorption with bromine-water before the treatment with cuprous chloride.

Temperature Measurements.

Throughout the whole of the present investigation, the temperatures have been estimated by a Wanner optical pyrometer. With a little practice this instrument can be made to give very concordant results. Little importance is attached to the absolute values of the temperature given, but some trouble was taken to ensure that they should be comparable with one another. Since the instrument was regularly calibrated by comparison with the amyl acetate lamp, the relative agreement of the temperature readings throughout the whole investigation may probably be relied on. No allowance has been made for the error in temperature indications, due to the fact that the simple laws of "black body" radiation do not strictly hold in the case of such heated rods.

Temperatures 1000° to 1700°.

A first series of more than fifty experiments was carried out in the apparatus previously described. The conditions of working varied somewhat greatly from case to case, as it was hoped in this way to obtain more definite evidence as to the course of the reaction.

As previously mentioned, for the purification of the carbon, reliance was placed on the evacuation of the containing vessel during the heating of the rod, on the continued use of the same rod in a number of consecutive experiments, and finally on frequently maintaining the carbon at a temperature of over 2000° in hydrogen, before the actual experimental run at the lower temperature.

There was at first no suspicion that the quantities of methane which were determined in these experiments were other than those corresponding to a definite equilibrium between carbon and hydro-

gen. On tabulating all the results, however, and carefully considering them in relation to the previous treatment of the carbon and to the actual conditions existing in the experiments, some discrepancies were brought to light; this can best be illustrated by the following examples:

TABLE I.

Experiment.	Time in mins. from start.	CO per cent.	CH ₄ per cent.
1	45	0.1	0.63
	120	0.2	0.77
	190	0.39	0.89
2	40	0.40	0.50
	230	0.32	0.65
	390	0.39	0.56

These two experiments were carried out under very similar conditions, but the rod in the first case had served in six, in the second case in fourteen previous runs; moreover, shortly before the latter experiment the carbon had been maintained for some time at over 2000° in hydrogen.

The result definitely indicates a lower methane formation with more complete preliminary treatment of the rod. This indication was fully borne out by many of the other experiments.

TABLE II.

Temperature of 1400°.

Experiment.	CO per cent.	CH ₄ per cent. at end of experiment.	
1	0.05	0.78	} Gas stood, in these cases, for two days over P ₂ O ₅ before experi- ment.
2	0.24	0.61	
3	—	0.43	
4	0.53	0.21	} Rod heated in a vacuum, in each case, for some time be- fore experiment.
5	0.47	0.21	

The two vacuum experiments seem to be particularly interesting, as the earlier samples taken for analysis all contain a considerably higher percentage of methane, which was evidently undergoing a progressive decomposition,* and tending towards a value which may be even lower than that given.

At higher temperatures (1700° to 1750°) the results were much more concordant, and the methane seldom exceeded 0.6 per cent.

* There can be no question of oxidation, since the percentage of carbon monoxide in these cases actually decreased.

In order to test the accuracy of these indications it was thought advisable to carry out a second series of experiments in which precautions were taken to ensure a more complete purification of the carbon.

For this purpose it was decided to heat the carbons to a high temperature in chlorine. The rods, held in graphite terminals, were supported in a glass flask, similar to that used in the experiments with hydrogen, through which chlorine was passed. The rod was in each case maintained at 1700—1800° for about one hour by the passage of an electric current. In this way, being considerably hotter than the surrounding atmosphere, it readily gave off the ash constituents as chlorides,* and the method in general has obviously a great advantage over the more usual one of heating in a glass or porcelain combustion tube.

The carbon rods after treatment in this manner were heated in a current of hydrogen, and subsequently mounted in the experimental apparatus previously described.

The accompanying tables give a record of the experiments carried out with these purified carbons. It will be seen that the percentage of methane shows a marked reduction in comparison with the values previously given.

Throughout the whole of the work, the greater the precautions which were taken to improve the quality of the carbon, the lower was the percentage of methane formed.

These results certainly favour the conclusion that with progressive purification of the carbon a still lower formation of methane would be found. Such experiments would, however, demand considerable refinement in the analytical methods, although with the Sodeau apparatus successive analyses can generally be relied on to within 0.04 per cent. It is not easy to explain the origin of the methane in the earlier experiments. Two hypotheses presented themselves, but neither could be confirmed.

Firstly, it might be supposed that on the cooler end-pieces carbon monoxide and hydrogen were caused to combine under the catalytic influence of iron or some other ash constituent, the preparation of methane under somewhat similar conditions having been carried out on an extensive scale by Sabatier and Senderens. An experiment in which equal volumes of carbon monoxide and hydrogen were maintained for fifteen hours in contact with a carbon rod heated to about 450° (just visible in a completely darkened room) failed, however, to produce more than 0.1 per cent. of methane.

Secondly, the existence of undecomposed hydrocarbon compounds

* The analysis of one of these rods before and after such treatment in chlorine gave an ash content of 0.25 per cent. and 0.07 per cent. respectively.

in the carbon rod seemed quite probable. To test this point the glass apparatus was fitted up with a fresh carbon rod, the air contained in the vessel was displaced by hydrogen, and then, with a mercury pump, a vacuum was obtained of below 1 mm. of mercury, the last traces of gas being collected for analysis. The rod was next heated in a vacuum, and the gas evolved carefully collected. The sample obtained before heating was almost pure hydrogen, free from measurable amount of oxygen, and containing only about 0·2 per cent. of carbon monoxide and less than 0·1 per cent. of methane. The second sample, obtained after heating, contained about 40 per cent. of carbon monoxide and less than 0·1 per cent. of methane.

The great power possessed by carbon of occluding carbon monoxide has already been described by Dewar and others; in this case, although it doubtless helps to account for the gradual increase in the carbon monoxide noticed in some of the previous experiments, it can scarcely give a simple explanation of the methane formation.

TABLE III.

Carbons Purified in Chlorine.

Experiment.	Temperature.	Time in minutes from start.	CO. per cent.	CH ₄ . per cent.
1	1350°	35	1·0	0·23
		90	1·7	0·20
2	1350	35	0·94	0·12
		90	1·5	0·25
3	1200	65	0·42	0·28
		120	0·37	0·20
4	1350	20	1·83	0·10
		60	3·6	0·25
5	1250	60	1·63	0·21
		90	1·7	0·25
6	1250	40	0·59	0·24

TABLE IV.

Temperature 1700°. Carbons Purified in Chlorine.

Experiment.	Time in minutes from start.	CO per cent.	CH ₄ per cent.
	20	1·0	0·42
2	15	2·92	0·36
	0	4·9	0·43
3	1	4·05	0·40

Temperatures 1800° to 2800°. Synthesis of Acetylene.

There is no great difficulty in applying the general experimental methods up to 2500° and over, if a good water-cooling of the terminals is assured. For these higher temperatures, as previously mentioned, the metal containing vessel is to be preferred. Owing to the expansion of the rods, and the marked plasticity which carbon possesses near the higher limits of temperature at which the experiments were carried out, it is necessary to provide some simple and efficient compensating device to prevent the bending of the rods from becoming excessive, and thus causing fracture.

The disintegration of the carbon becomes somewhat great, and accounts for the short duration of many of these experiments, but on the other hand the equilibrium is rapidly attained.

Except in the presence of considerable amounts of carbon monoxide the apparent vaporisation of carbon is not very marked even at the highest temperatures reached, the disintegration previously referred to being more of the nature of a crumbling away of the rod, causing its surface to become very rough. The remarkable uniformity of temperature throughout almost the whole length of the rod may doubtless be explained by the fact that such portions as tend to have a lower temperature offer a greater electrical resistance, and consequently demand a greater expenditure of energy.

The chief experiments are tabulated in Table V, from which the gradual increase in the percentage of acetylene with increase of temperature can be clearly seen. The formation of minute quantities of acetylene at 1700° can just be detected by the delicate cuprous chloride test, but the percentage is scarcely measurable by ordinary gas-analysis methods below 1800°.

The formation of acetylene at these low temperatures, and independently of an electric arc or spark discharge, has not previously been noted so far as can be ascertained. The temperature of the positive crater of the carbon arc is at the present time estimated at between 3500° and 3750°. Moreover, in gaseous reactions effected with the arc, the electrical conditions doubtless intervene and complicate the study of the question.

TABLE V.

Experiments at 1870° to 2800°.

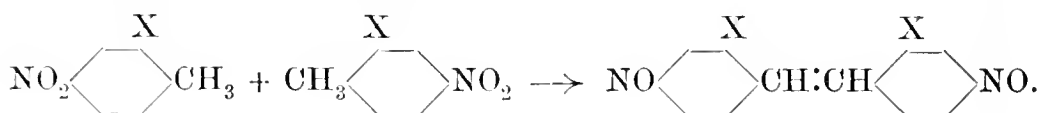
Experiment.	Temp.	Time in minutes from start.	CO.	CH ₄ .	C ₂ H ₂ .	Observations.
1	1870°	9	1.8	0.55	0.42	
		24	2.48	0.64	0.26	
		40	2.45	0.93	0.35	
2	1900	8	2.1	0.68	0.35	
		17	2.1	0.18	0.26	
3	1960	10	6.4	0.51	{ 0.55 0.70	
4	1975	5	2.7	0.54	0.27	
5	2000	10	6.67	0.47	0.34	
		20	8.25	0.63	0.55	
6	2000	10	3.61	0.39	0.87	{ Rod specially purified with chlorine.
		16	4.72	0.49	0.88	
7	2000	3	3.9	0.50	0.96	
8	2050	7	3.7	0.70	0.94	
		12	4.2	0.62	0.92	
9	2105	5	1.72	0.55	0.85	
10	2135	5	5.73	0.54	0.95	
		10	6.3	0.53	1.44	
11	2170	2	10.0	0.56	1.45	
		6½	12.0	0.69	1.40	
		13	13.9	0.51	1.08	
12	2400	4	3.68	0.83	3.26	
13	2465	1	9.0	1.01	2.60	
14	2500	4	6.42	1.20	4.20	
15	2500	1½	9.0	0.96	3.64	
16	2500	2½	4.1	1.26	{ 3.68 3.35	
		3½	4.42	1.20	3.40	
17	2540	2	6.0	0.89	2.12	
18	2700	2	0.62	1.05	3.03	
19	2700	2	1.81	1.07	3.05	
20	2700	2	5.7	1.05	2.75	
21	2800	1	4.1	0.68	2.73	{ Equilibrium probably not attained. N.B. low methane.

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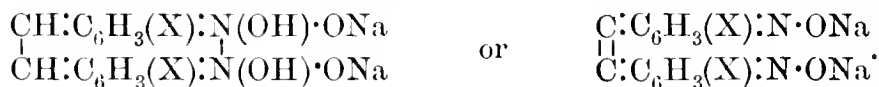
CLXII.—*The Colouring Matters of the Stilbene Group. Part III.*

By ARTHUR GEORGE GREEN and PERCY FIELD CROSLAND.

IN previous communications on this subject (Green and Wah, *Ber.*, 1897, **30**, 3097; 1898, **31**, 1078; Green, *Trans.*, 1904, **85**, 1424; Green, Marsden, and Scholefield, *Trans.*, 1904, **85**, 1432) a study has been made of the first stage of the reaction by which *p*-nitrotoluene and its ortho-substituted derivatives give rise to stilbene compounds. It was shown that under the influence of caustic alkalis an internal oxidation takes place with the production of dinitrostilbene (or a derivative thereof):



These nitrostilbenes are very unstable products, possessing in alkaline solution a deep crimson, violet, or blue colour, in which condition their salts probably have the tautomeric quinonoid structure:



These coloured salts are easily oxidised by air or by alkali hypochlorites to the corresponding dinitrostilbene derivatives:



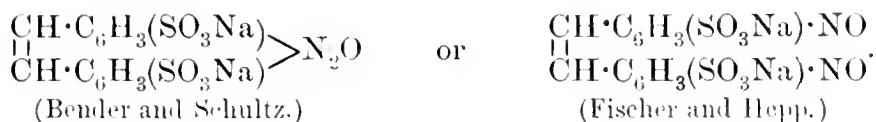
and, inversely, from the latter they are readily reproduced by the action of cold alkaline reducing agents.

On further condensation of these nitroso-compounds by longer heating with caustic alkalis, stilbene dyestuffs are produced. Thus in the technically important case of *p*-nitrotoluenesulphonic acid, this compound gives on warming with aqueous sodium hydroxide a crimson-red solution of the dinitrostilbenedisulphonate (X in above formulæ = SO₃Na), which on further heating becomes orange-yellow with production of Direct Yellow or Curcumine S. Similar, but purer, dyestuffs (so-called "Stilbene Yellows") are obtained from dinitrostilbenedisulphonic acid by alkaline reduction, the same red compound being an intermediate stage of the reaction. The yellow dyestuffs obtained by either method, when submitted to further reduction in

alkaline solution, are transformed progressively into reddish-yellow, yellowish-orange, and reddish-orange dyestuffs, then into leuco-compounds (readily reoxidising to orange), and finally into diaminostilbenedisulphonic acid. This progressive reduction is accompanied by a change in the colour of the solution in concentrated sulphuric acid from orange-red, through crimson and violet, to pure blue.

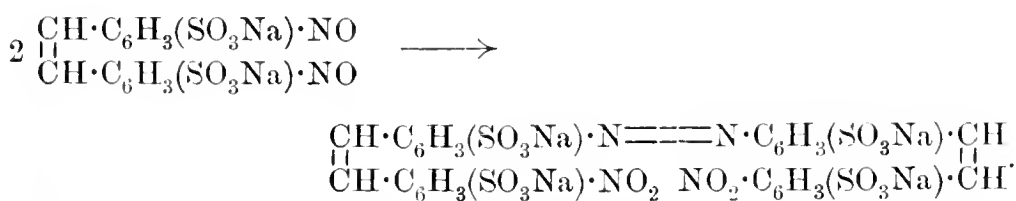
The present paper deals with the second stage of the colour formation, namely, that by which the dyestuffs are produced from the intermediate dinitrostilbenedisulphonic acid.

It is generally considered that the yellow condensation product (Direct Yellow or Curcumine) is a disulphonic acid of a simple azoxy- or dinitroso-stilbene :



The improbability of either of these formulæ has already been discussed in a former communication, and against the second there is now the further objection that it is required for the intermediate unstable crimson compound. Moreover, grounds have been adduced for believing that the molecule of these dyestuffs must contain at least two stilbene groups, that is, that a coalition of at least four molecules of *p*-nitrotoluene must occur in their formation.

It seemed possible that this condensation might take place through the oxidation of one nitroso-group at the expense of the other, the remaining nitrogen atoms of two molecules uniting together to form an azo-group :



If this view is correct the above equation will represent the formation of the greenest yellow of the series (Stilbene Yellow 8G). The redder yellows and oranges might then be regarded as formed therefrom by reduction of the two nitro-groups, first to an azoxy-, and finally to an azo-group.

To test this hypothesis we have made use of the following analytical methods :

A. Estimation of the quantity of hydrogen required for reducing the dyestuffs to diaminostilbenedisulphonic acid, employing for this purpose titration with standard titanium trichloride (Knecht, *J. Soc. Dyers*, 1903, 19, 169 ; 1905, 21, 292).

B. Estimation of the ethylene groups by determining the quantity of standard permanganate required to oxidise the dyestuffs to aldehydes in cold dilute aqueous solution (Green and Meyenberg, Eng. Pat., 1431 of 1898). As the oxidation takes place in absence of acid, 2 molecules of permanganate are equivalent to $1\frac{1}{2}$ ethylene groups.

C. Direct estimation of the aldehyde groups produced in *B* by titration with a standard solution of phenylhydrazine.

D. Isolation and characterisation of the aldehyde compounds obtained.

The reliability of methods *A*, *B*, and *C* was checked by applying them to pure preparations of dinitrostilbenedisulphonic acid and of Chrysophenine G, with which compounds satisfactory results were obtained.

In the experiments which follow we have selected as typical stilbene dyestuffs, Direct Yellow RT (Clayton), Stilbene Yellow 8G and 4G (Clayton), and Mikado Orange (Leonhardt). These dyestuffs after suitable purification gave results which fully confirm the above hypothesis. Stilbene Yellow 4G and 8G proved to consist almost entirely of dinitroazodistilbenedisulphonic acid. Direct Yellow is less pure, but appears to consist substantially of azoxyazodistilbenedisulphonic acid mixed with some quantity of an azomethine by-product. Mikado Orange 3RO, which could not be obtained entirely pure, gave results which approximate to those required for the disazodistilbenedisulphonic acid. It also contains considerable quantities of an azomethine dyestuff, which is still under investigation.

All these dyestuffs are therefore azo-compounds, and their chromophore is doubtless the azo-group. This explains their dyeing properties, which, if regarded as azoxy- or nitroso-compounds, would be difficult to account for. Only in one particular is their constitution peculiar, namely, in the fact that they possess no auxochrome group. This, however, is less remarkable than it would have appeared formerly, for an increasing number of dyestuffs is becoming known (for example, Chrysophenine, Diamine Golden-yellow, &c.), in which no special auxochrome group occurs, and the view is gaining ground that the action of such groups (OH, NH₂, NMe₂, &c.) is to be attributed to their calling forth a more stable quinonoid structure rather than, as was formerly believed, to their salt-forming functions. Such strongly salt-forming groups as SO₃H and NMe₃OH have no auxochrome effect.

Stilbene Yellow 8G (Clayton).

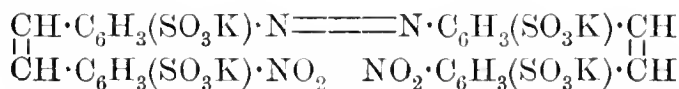
This colouring matter is prepared by heating dinitrostilbenedisulphonic acid in caustic alkaline solution at 80°, with the minimum quantity of glucose necessary to effect reduction. A very similar pro-

duct chemically, but of a much less degree of purity, is obtained by the oxidation of Direct Yellow with sodium hypochlorite (Mikado Golden-yellow). For the complete purification of Stilbene Yellow 8G the dye-stuff was converted into the potassium salt by precipitation with potassium chloride from a boiling aqueous solution. The precipitate was redissolved and the process repeated two or three times. Finally, it was washed with 50 per cent. alcohol to remove potassium chloride. By this means the colouring matter is obtained as a scarlet, crystalline powder.

Reduction.—The quantitative reduction with titanium trichloride is carried out in the manner described by Knecht (*loc. cit.*), employing the indirect method, namely, running in an excess and titrating back with standard ferric sulphate. For each experiment 0.1 gram of dye-stuff was employed, which was dissolved in 100 c.c. of water and strongly acidified with hydrochloric acid. The solution was boiled until free from air, and while carbonic acid gas was led in, a small excess of titanium trichloride added. After boiling for a minute, the solution was cooled and the excess of titanium trichloride titrated back with ferric sulphate solution, using ammonium thiocyanate as indicator. In applying this method to the stilbene dyestuffs it was found necessary to employ only a small excess of titanium trichloride. If a large excess is used, the reduction proceeds beyond diaminostilbenedisulphonic acid, and diaminodibenzylidisulphonic acid is obtained. This was definitely proved with dinitrostilbenedisulphonic acid, which we found could be reduced either to diaminostilbenedisulphonic acid or to diaminodibenzylidisulphonic acid according to the amount of titanium trichloride employed. The following are the results obtained with pure Stilbene Yellow 8G :

No. of experiment.	Weight of dyestuff (1 c.c. = 0.00003085 gram H).	Vol. of TiCl_3 run in (gram H).	Vol. of TiCl_3 used.	Percentage loss of H_2O on drying at 150° .	Percentage of hydrogen on dry dyestuff.
1	0.1	60 c.c.	51.4 c.c.	1.6	1.66
2	0.1	57 „	52.6 „	1.6	(mean of
3	0.1	56 „	53.2 „	1.6	last three
4	0.1	57 „	53.0 „	1.6	experiments)

The compound,



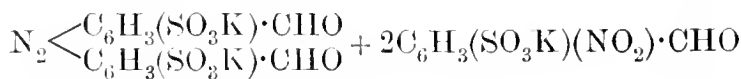
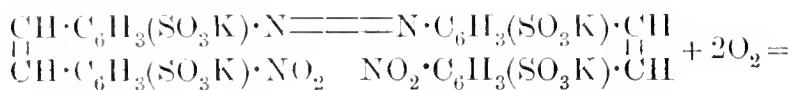
requires for reduction to diaminostilbenedisulphonic acid 1.69 per cent. of hydrogen.

Oxidation.—The titration of stilbene dyestuffs with potassium permanganate is carried out in the following way: 0.15 to 0.2 gram of the dyestuff is dissolved in 150 c.c. of water, the solution thoroughly

cooled, and a volume of standard permanganate, about three-quarters of the total quantity required, is slowly run in. The mixture is then heated to precipitate the colloidal manganese dioxide and filtered. The filtrate and washings are concentrated to about half the former bulk, cooled, and the titration completed by slowly adding a solution of potassium permanganate one-quarter the strength of that first used. The end-point is reached when two or three drops of the liquid, after salting out manganese dioxide with potassium chloride, retain a pale pink colour. The following results were obtained with pure Stilbene Yellow 8G:

No. of experiment.	Weight of dyestuff in grams.	Vol. of KMnO ₄ required (1 c.c. = 0.000166 gram O).	Percentage loss of H ₂ O on drying at 150°.	Percentage of oxygen on dry dyestuff.
1	0.2	28.9 c.c.	1.6	} 6.84 (mean value)
2	0.2	28.8 "	1.6	
3	0.2	29.0 "	1.6	
4	0.2	28.9 "	1.6	

The equation



requires 6.75 per cent. of oxygen.

Separation and Examination of Oxidation Products.—Thirty-eight grams of pure Stilbene Yellow 8G were dissolved in 2000 c.c. of water. The solution was cooled with ice and oxidised with a cold solution of 16.8 grams of potassium permanganate in 2000 c.c. of water which was slowly run in. After heating to coagulate the manganese dioxide, the solution was filtered, neutralised with hydrochloric acid, and concentrated to a small bulk. On cooling, the product separated as a semicrystalline, pale yellow solid. This proved to be a mixture of the potassium salts of *nitrobenzaldehydesulphonic acid* and of *azobenzaldehydesulphonic acid*. The latter substance could be separated from the mixture by making use of its less solubility in dilute alcohol or in aqueous solutions of potassium chloride. The nitrobenzaldehydesulphonate was obtained in our earlier experiments by extracting the mixture with absolute alcohol, in which it is slightly soluble, whilst the azobenzaldehydesulphonate remains undissolved. A better method, found later, consists in making use of the different behaviour of the two aldehydes towards benzidine in an aqueous solution rendered acid with hydrochloric acid. Under these conditions, only the azoaldehyde combines, and after separating the insoluble dark brown azomethine compound, and removing excess of benzidine with potassium sulphate,

the nitroaldehyde can be obtained as potassium salt from the neutralised and concentrated filtrate. This method of separation is so sharp that by employing a 1 per cent. solution of benzidine hydrochloride it is possible to titrate the amount of azoaldehyde in a given mixture, especially if *p*-aminodiphenylamine is used as indicator. The latter base gives in acid solution an insoluble, dark violet-blue precipitate (azomethine condensation product) with the azoaldehyde, but little or no coloration with the nitroaldehyde. Also, with other bases, the two aldehydes behave differently. Thus, in mineral acid solution *p*-phenylenediamine gives, with the azoaldehyde, a reddish-brown azomethine compound, but no coloration with the nitroaldehyde. The phenylhydrazone of the azoaldehyde is reddish-brown, whilst that of the nitroaldehyde is orange. On alkaline reduction, the two aldehydes also show distinctive reactions; thus when a particle of zinc dust is added to a solution of the azoaldehyde mixed with an excess of sodium hydroxide, a litmus-blue coloration is obtained, whilst under the same conditions the nitroaldehyde only gives a yellow colour.

Potassium 4-nitrobenzaldehyde-2-sulphonate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{K}) \cdot \text{CHO}$, was obtained, as above described, in the form of slender, colourless needles or stout prisms. It gave identically the same reactions as the product obtained by the oxidation of dinitrostilbenedisulphonic acid (Green and Wahl, *Ber.*, 1897, 30, 3097). On heating, it decomposes suddenly. Analysis gave:

Found, N = 5.5 and 5.4; S = 11.74 and 11.94.

$\text{C}_7\text{H}_4\text{O}_6\text{NSK}$ requires N = 5.2; S = 11.9 per cent.

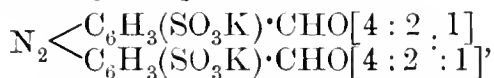
Reduction with titanium trichloride gave the following results:

Hydrogen used, 2.17, 2.17, and 2.21.

$\text{C}_7\text{H}_4\text{O}_6\text{NSK}$ requires hydrogen used = 2.23 per cent.

(The substance used in the last reduction was a purer preparation.)

Potassium azobenzaldehydesulphonate,



was obtained as a buff, crystalline solid, which appears to exist in two modifications. One of these is easily soluble, the other somewhat sparingly so in cold water. The colour reactions of this aldehyde, which have already been described, are very characteristic. With a large variety of primary bases, it readily gives azomethine compounds. Analysis gave:

N = 6.05 and 5.94.

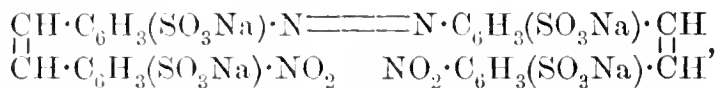
$\text{C}_{14}\text{H}_8\text{O}_8\text{N}_2\text{S}_2\text{K}_2$ requires N = 5.91 per cent.

Reduction with titanium trichloride gave the following results

Hydrogen required (mean of two experiments) = 0.87. Theory requires H = 0.84 per cent.

Stilbene Yellow 4G (Clayton).

This dyestuff is prepared in a very similar way to the 8G brand, only the reduction is carried a little further by employing somewhat more glucose in order to obtain a rather redder shade. The following experiments show that, like the 8G brand, it consists substantially of the dinitroazodistilbenedisulphonate,



though containing in addition a small quantity of the corresponding azoxyazo-compound. The purification was conducted in the same way as above described. The pure potassium salt of the dyestuff was obtained as a scarlet, semi-crystalline powder.

Reduction.—Same method as used above.

No. of experiment.	Weight of dyestuff in grams.	Vol. of TiCl_3 run in (1 c.c. = 0.000046 gram H).	Vol. of TiCl_3 used.	Percentage loss of H_2O on drying at 150° .	Percentage of hydrogen on pure dyestuff.
1	0.1	37.3 c.c.	34.7 c.c.	1.5	} 1.61 (mean value)
2	0.1	39.9 „	34.6 „	1.5	
3	0.1	50.0 „	34.4 „	1.5	
4	0.1	35.4 „	34.3 „	1.5	
5	0.1	35.4 „	34.4 „	1.5	

The theoretical quantity of hydrogen required by potassium dinitroazodistilbenedisulphonate for its reduction to diaminostilbenedisulphonic acid is 1.69 per cent.

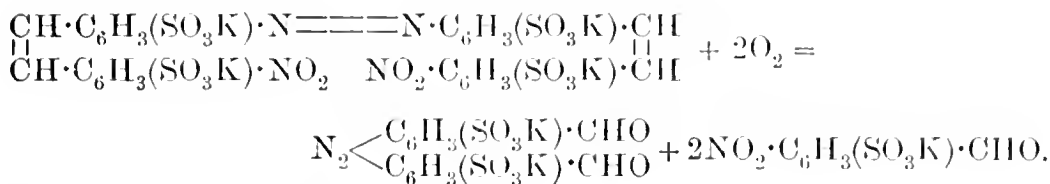
Oxidation.—Same method as above mentioned.

No. of experiment.	Weight of dyestuff in grams.	Vol. of KMnO_4 required (1 c.c. = 0.000662 gram O).	Percentage loss of H_2O on drying at 150° .	Percentage of oxygen on dry dyestuff.
1	0.1	9.7 c.c.	5.7	} 6.85 (mean value)
2	0.1	9.85 „	5.7	
3	0.1	9.75 „	5.7	
4	0.1	9.8 „	5.7	
5	0.1	9.7 „	5.7	

Another series of determinations made with a different permanganate solution and another preparation of the dyestuff gave the following results :

No. of experiment.	Weight of dyestuff in grams.	Vol. of KMnO_4 required (1 c.c. = 0.000466 gram O).	Percentage loss of H_2O on drying at 150° .	Percentage of oxygen on dry dyestuff.
6	0.2	29.0 c.c.	1.6	} 6.85 (mean value)
7	0.2	29.1 "	1.6	
8	0.2	28.8 "	1.6	
9	0.2	28.8 "	1.6	

The equation



requires 6.75 per cent. of oxygen.

Separation and Examination of the Oxidation Products.—A quantity of Stilbene Yellow 4G (sodium salt) was oxidised with the theoretical quantity of potassium permanganate in cold dilute aqueous solution in the manner already described on page 1605. The solution after filtration from manganese dioxide, neutralisation, and concentration, gave a product which proved to be a mixture of the two aldehydes, whose formation is indicated by the foregoing equation.

Sodium nitrobenzaldehydesulphonate was obtained as a colourless, crystalline powder by extracting the above mixture of the sodium and potassium salts of the two aldehydes with absolute alcohol. It gave the same reactions as the product obtained from the 8G colouring matter, and as nitrobenzaldehydesulphonic acid prepared from dinitrostilbenedisulphonic acid. On analysis:

$\text{N} = 5.7$ and 5.55 .

$\text{C}_7\text{H}_4\text{O}_6\text{NSNa}$ requires $\text{N} = 5.54$ per cent.

The azobenzaldehydesulphonic acid was obtained as the potassium salt from the crude aldehyde mixture by submitting the latter to a series of fractional precipitations from aqueous solution, first by means of alcohol and later by means of potassium chloride. Finally, to remove traces of the latter salt, the product was washed with 50 per cent. alcohol. The potassium salt is thus obtained as an easily soluble buff, crystalline powder which exhibits all the reactions already described. Analysis gave:

$\text{N} = 5.94$ and 5.78 ; $\text{S} = 13.26$ and 13.28 ; $\text{K} = 16.36$ and 16.99 .

$\text{C}_{14}\text{H}_8\text{O}_8\text{N}_2\text{S}_2\text{K}_2$ requires $\text{N} = 5.90$; $\text{S} = 13.50$; and $\text{K} = 16.46$ per cent.

Reduction with titanium trichloride gave the following results:

Hydrogen required (mean of 4 determinations) = 0.81.

Theory requires 0.85 per cent.

Direct Yellow RT (Clayton).

The colouring matters which occur in commerce under the names of Direct Yellow, Curcumine S, Sun Yellow, and Naphthamine Yellow are obtained by heating *p*-nitrotoluenesulphonic acid with an excess of sodium hydroxide for several hours at temperatures between 60° and 80°. We have selected for examination the RT brand of the Clayton Aniline Co. Commercial Direct Yellow is a far less pure product than the Stilbene Yellows already dealt with. It always contains in addition to other impurities considerable quantities of an azomethine compound. This by-product, which is also a yellow dyestuff, reacts with phenyl hydrazine giving an orange hydrazone. Moreover, by the action of nitrous acid it yields a diazo-compound which gives red dyestuffs when combined with β -naphthol. These reactions are readily performed on the cotton fibre dyed with commercial Direct Yellow. The removal of this by-product, which appears to be constituted analogously to Curcuphenine (Trans., 1904, 85, 1426), is extremely difficult, and necessitates a somewhat tedious purification. For this purpose the dyestuff was precipitated as the sparingly soluble calcium salt, which was repeatedly extracted with large quantities of boiling water, and then converted into the potassium salt by boiling with potassium carbonate. From the solution the potassium salt was salted out by the addition of potassium chloride, redissolved, and salted out afresh several times. The colouring matter was then dried, powdered, and, in order to remove potassium chloride, washed with 50 per cent. alcohol and again dried ("Preparation A"). Another method of purification employed consisted in treating the dyestuff in acid solution with a small quantity of sodium nitrite (10 grams required 1 c.c. of *N*/1 NaNO_2), followed by phenyl hydrazine in equivalent quantity, in order to decompose and remove the azomethine by-product. The dyestuff was then repeatedly dissolved and reprecipitated with potassium chloride, finally washed with dilute alcohol and dried ("Preparation B").

Reduction.—Same method as used above. The following results were obtained with preparation A :

No. of experiment.	Weight of dyestuff in grams.	Vol. of TiCl_3 run in (1 c.c. = 0.0000888 gram H).	Vol. of TiCl_3 used.	Percentage loss of H_2O on drying at 150°.	Percentage of Hydrogen on dry dyestuff.
1	0.1	13.5 c.c.	11.0 c.c.	7	} 1.08 (mean value)
2	0.1	13.5 "	11.0 "	7	
3	0.1	14.0 "	11.8 "	7	
4	0.1	13.8 "	11.4 "	7	

The following results were obtained with preparation B and employing another titanium solution :

No. of experiment.	Weight of dyestuff in grams.	Vol. of TiCl_3 run in (1 c.c. = 0.0001063 gram H).	Vol. of TiCl_3 used.	Percentage loss of H_2O on drying at 150° .	Percentage of Hydrogen on dry dyestuff.
5	0.1	12.2 c.c.	8.85 c.c.	12	} 1.08 (mean value)
6	0.1	10.9 "	9.3 "	12	
7	0.1	11.1 "	8.7 "	12	

The azoxyazodistilbenedisulphonate,



O

requires for reduction to diaminostilbenedisulphonic acid 1.11 per cent. of hydrogen. Considering the difficulty of complete purification, the above results agree sufficiently closely with this formula.

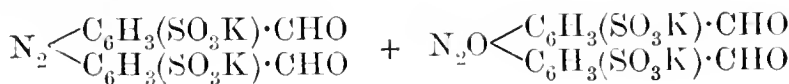
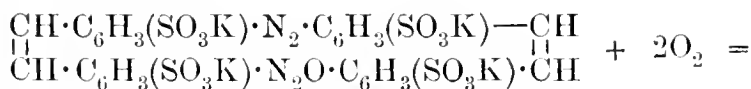
Oxidation.—Same method as used above. The following results were obtained with preparation A :

No. of experiment.	Weight of dyestuff in grams.	Vol. of KMnO_4 required (1 c.c. = 0.001324 gram O).	Percentage loss of H_2O on drying at 150° .	Percentage of oxygen on dry dyestuff.
1	0.15	7.4 c.c.	5.4	} 7.0 (mean value)
2	0.15	7.5 "	5.4	
3	0.15	7.6 "	5.4	

The following results were obtained with preparation B and employing another permanganate solution :

No. of experiment.	Weight of dyestuff in grams.	Vol. of KMnO_4 required (1 c.c. = 0.000465 gram O).	Percentage loss of H_2O on drying at 150° .	Percentage of oxygen on dry dyestuff.
4	0.15	20.9 c.c.	5.4	} 6.8 (mean value)
5	0.15	20.3 "	5.4	
6	0.15	20.5 "	5.4	

The equation



requires 7.1 per cent. of oxygen.

Examination of the Oxidation Products.—We have not yet effected a separation of the two aldehydes indicated by the above equation. The mixture, however, gives the characteristic colour reactions of the azo-benzaldehydedisulphonic acid when treated with phenylhydrazine, *p*-phenylenediamine, benzidine, *p*-aminodiphenylamine, and also with zinc dust in presence of sodium hydroxide. In order to estimate the

aldehyde groups in the product, the mixed aldehydes were titrated with a standard solution of phenylhydrazine hydrochloride. For this purpose the Direct Yellow was oxidised with a slight deficiency of permanganate, and, after removing the non-oxidised colour with barium chloride, the filtrate was concentrated and the mixed aldehydes salted out with potassium chloride and washed with 50 per cent. alcohol. The product, dried at 140° , was dissolved in hot water with addition of sodium acetate and titrated with a solution of phenylhydrazine hydrochloride containing 11.1 grams of the base per 1000 c.c. The end-point is indicated by a spot on paper giving a red margin when brought in contact with a drop of azobenzaldehydesulphonic acid solution.

No. of experiment.	Weight of mixed aldehyde taken in grams.	Vol. of phenylhydrazine solution.	Percentage of phenylhydrazine required.
1	0.213	7.5 c.c.	39.0
2	0.203	7.8 "	42.6

A mixture in equimolecular quantities of the potassium salts of azobenzaldehydesulphonic acid and azoxybenzaldehydesulphonic acid would require theoretically 44.8 per cent. of phenylhydrazine. The method can only be regarded as approximate as the end-point is rather difficult to see, but the result confirms the above equation for the oxidation of the dyestuff.

Mikado Orange (Leonhardt).

Various brands of this dyestuff are prepared either by condensing *p*-nitrotoluenesulphonic acid with sodium hydroxide in the presence of reducing agents or by submitting the condensation product (Direct Yellow) to alkaline reduction. The most completely reduced product appears to be the 3RO brand, the 4RO and 5RO brands being probably mixtures of the former with a red dyestuff. Most of our experiments were performed with the 3RO, but some with the 4RO and 5RO brands, from which the red dyestuff was removed. It was found that all these dyestuffs contained a large quantity of an azomethine by-product. The presence of this compound is readily shown by the fact that on treatment of the acid solution of the dyestuff with sodium nitrite a portion of it is decomposed into a diazo-compound, which gives a red colour with β -naphthol, and an aldehydic compound, which gives a dark brown hydrazone with phenylhydrazine. Although we have employed a variety of purification methods we have hitherto been unable entirely to remove this by-product and thus obtain the Mikado Orange in a pure state. By repeated fractional precipitation with potassium chloride and dilute alcohol, the quantity

of the by-product present, as shown by the above tests, continually diminishes, and simultaneously therewith the numbers obtained on reduction with titanium trichloride approximate more and more to those required for the formula



We are continuing the investigation and hope later to obtain the colouring matter in a completely pure state.

The following results were obtained with the potassium salt of Mikado Orange 3RO, after several precipitations with potassium chloride and alcohol :

Reduction.—Same method as used before.

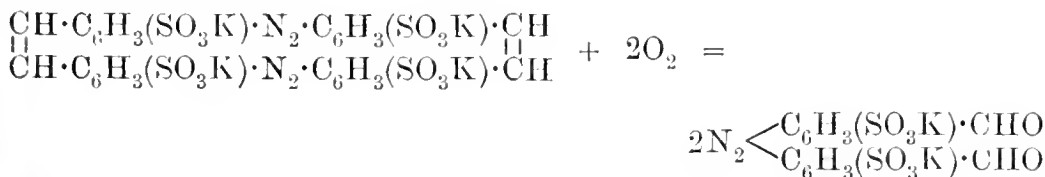
No. of experiment.	Weight of dyestuff in grams.	Vol. of TiCl_3 run in (1 c.c. = 0.00007392 gram H).	Vol. of TiCl_3 used.	Percentage loss of H_2O on drying at 150° .	Percentage of hydrogen on dry dyestuff.
1	0.1	14.3 c.c.	9.8 c.c.	2.1	} 0.74 (mean value)
2	0.1	14.65 „	9.75 „	2.1	
3	0.1	14.05 „	9.85 „	2.1	

The theoretical quantity of hydrogen required for the potassium salt of disazodistilbenedisulphonic acid of the above constitution is 0.90. The experimental results are therefore 82 per cent. of the theoretical.

Oxidation.—Same method as used before.

No. of experiment.	Weight of dyestuff in grams.	Vol. of KMnO_4 required (1 c.c. = 0.000605 gram O).	Percentage loss of H_2O on drying at 150° .	Percentage of oxygen on dry dyestuff.
1	0.1	11.5 c.c.	2.1	} = 7.1 (mean value)
2	0.1	11.5 „	2.1	
3	0.1	11.45 „	2.1	
4	0.1	11.5 „	2.1	

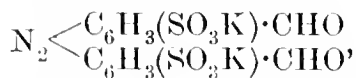
The equation



requires 7.24 per cent. of oxygen.

From the product of the oxidation of commercial Mikado Orange 3RO with permanganate in cold dilute aqueous solution we were able to isolate two aldehyde compounds: (a) a very sparingly soluble well-crystallising substance; (b) an easily soluble compound. The first gave a very sparingly soluble red phenylhydrazone, and is apparently

an oxidation product of the azomethine by-product. The second gave the reactions of azobenzaldehydesulphonic acid,



the formation of which is indicated by the above equation.

Our thanks are due to the Clayton Aniline Co., Ltd., and to the Farbwerk Mülheim for kindly supplying us with the dyestuffs examined.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
UNIVERSITY OF LEEDS.

CLXIII.—*The Explosive Combustion of Hydrocarbons. II.*

WILLIAM ARTHUR BONE, JULIEN DRUGMAN, and GEORGE WILLIAM ANDREW.

IN a previous paper on this subject (this vol., p. 660) we discussed the results of a series of experiments on the propagation of a flame under ordinary conditions ("inflammation") through mixtures of typical hydrocarbons with amounts of oxygen insufficient for complete combustion, from which it was argued that there is no essential difference between the mechanism of combustion above and below the ignition point, inasmuch as both phenomena involve the initial formation of hydroxylated molecules.

The proof of this proposition depended chiefly on two sets of facts, namely:

(1) The remarkable contrast between the behaviour of an olefine and that of the corresponding paraffin when exploded with a proportion of oxygen represented by the expression $\text{C}_x\text{H}_y + x/2\text{O}_2$, and (2) the phenomena associated with the inflammation of a mixture of an olefine with much less oxygen than this expression requires, for example, $3\text{C}_2\text{H}_4 + 2\text{O}_2$.

Having established these main facts, it seemed important to investigate the behaviour of mixtures of ethane and oxygen, and ethylene and oxygen, corresponding to $\text{C}_2\text{H}_6 + \text{O}_2$ and $3\text{C}_2\text{H}_4 + 2\text{O}_2$ respectively, by a method which would allow of some discrimination between the various combustion products, according as they arise at an earlier or later stage in the flame. The method consisted in a careful comparison of the phenomena associated with the passage of a flame through a given explosive mixture sealed up in glass vessels of gradually diminishing surface area per unit volume, the argument being that, provided

the whole of the mixture is actually "inflamed," the primary products will tend to accumulate the more the flame is subjected to the cooling influence of the walls of the containing vessel, and, conversely, will be more and more replaced by secondary products as this cooling action is diminished. These experiments have yielded very interesting results, which are entirely in accordance with the theory advanced in the previous paper.

Hitherto we have refrained from discussing the subject of "detonation," except quite incidentally in connexion with other matters, because of the difficulty of obtaining any crucial evidence as between our own views and other possible theories. Experiments on the detonation of an equimolecular mixture of ethylene and oxygen, or of acetylene and oxygen (see Lean and Bone, *Trans.*, 1892, **61**, 873, and Bone and Cain, *Trans.*, 1897, **71**, 26), afforded no crucial data, because the results obtained can be explained either by our theory or on the supposition of a preferential burning of carbon. Since the publication of our last paper, however, we have succeeded in setting up "detonation" in mixtures of ethane and oxygen and butane and oxygen, corresponding to $C_2H_6 + O_2$ and $C_4H_{10} + 4O_2$ respectively.

The results obtained enable us to advance the main question a stage further, inasmuch as they indicate that there is probably no essential difference between "*detonation*" and "*inflammation*," so far as the result of the initial encounters between individual molecules of hydrocarbon and oxygen is concerned. In other words, the new facts afford an experimental basis for the belief that the theory outlined in our previous paper truly represents the mechanism of "detonation" as well as of ordinary "inflammation."

I. *Discrimination between the Various Products obtained in Ordinary Hydrocarbon Flames.*

These experiments were all carried out with mixtures of either ethane and oxygen, or ethylene and oxygen, corresponding to $C_2H_6 + O_2$ and $3C_2H_4 + 2O_2$ respectively. For the sake of brevity, we shall confine our remarks to a series of typical comparative experiments with each mixture in which three different vessels were employed, since they bring out very clearly all the salient features of our results. In each experiment, the mixture under investigation was inflamed in one of the three following vessels:

A. *Spherical Glass Globe* of stout borosilicate glass, internal diameter = 8.5 cm., volume = 320 c.c. The mixture was ignited by a spark at the centre of the vessel. The area of the internal walls = 226 sq. cm., and the ratio $\frac{\text{Cooling surface}}{\text{Volume}}$, hereafter called the "*cooling factor*," = 0.7.

B. Borosilicate Glass Cylinder. Length = 1.5 metres, internal diameter = 20 mm., volume = 470 c.c., area of cooling walls = 940 sq. cm., and "cooling factor" = 2.0.

The mixture was fired by a spark passed between wires at one end of the cylinder, and the flame travelled down its whole length and was finally extinguished at the other end.

C. Borosilicate Glass Cylinder. Length = 0.67 metre, internal diameter = 12.5 mm., volume = 80 c.c., area of cooling walls = 250 sq. cm., and "cooling factor" = 3.0. As in the previous case, the mixture was inflamed by a spark at one end of the cylinder.

Each of the vessels was provided with suitable inlet and outlet tubes of capillary bore, which facilitated the sealing up of the whole arrangement after the gases had been introduced at the desired experimental pressure, a very necessary precaution against loss of gas during the explosive combustion.

In tabulating the various results we shall make use of :

p_1 = initial pressure of the "nitrogen-free" original mixture before firing.

p_2 = final pressure of the "nitrogen-free" cold products.

(i) *Experiments with an Equimolecular Mixture of Ethane and Oxygen.*

$\text{C}_2\text{H}_6 = 49.5$ and $\text{O}_2 = 50.5$ per cent.

In the case of this mixture it will only be necessary to consider the results of typical comparative experiments with the larger globe, *A*, and the long cylinder, *B*, respectively, because the enhanced cooling effect obtained in passing from *B* to the narrower cylinder, *C*, usually brought about the extinction of the flame after it had travelled a short distance from its origin.

(a) When the mixture was fired in the long cylinder, *B*, at an initial pressure of 701 mm., a bright flame slowly travelled down its whole length at a rate of half a metre per second. There was no sign of anything approaching "detonation," but the whole of the mixture was actually inflamed, and from a photographic record it was estimated that each successive layer of gas remained incandescent for from $\frac{1}{20}$ th to $\frac{1}{30}$ th of a second. Some carbon separated in the flame, and much water condensed on cooling. The ratio p_2/p_1 was 1.45, and on subsequently rinsing out the cylinder with distilled water, and applying Schiff's test to the rinsings, a very strong aldehydic reaction was obtained. The gaseous products contained as much as 5.0 per cent. of acetylene and 2.65 per cent. of ethylene.

(b) In the comparative experiment with the large globe, at an

initial pressure of 651 mm., a lurid flame instantly filled the vessel. There was a much greater separation of carbon than was observed with the cylinder, but less water condensed on cooling. The ratio p_2/p_1 was now as high as 1.73, a clear indication that the longer duration of the flame had increased the yield of gaseous products at the expense of steam and aldehydes. Another noticeable feature about the results was the very small quantity of acetylene and ethylene, 0.15 per cent. only, in the gaseous products. On applying Schiff's test to the rinsings, a much fainter aldehydic reaction was obtained than in the previous experiment, although it was still quite distinct.

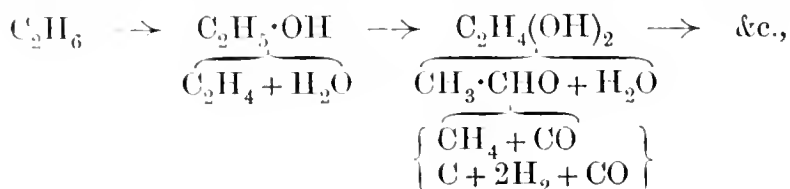
The influence of "cooling" was further demonstrated in another way by repeating the experiment with the globe at a much lower initial pressure (448 mm.), when, of course, the flame temperature would be lower. The flame again filled the bulb, much carbon separated, but more water, aldehydes, and unsaturated hydrocarbons were formed than at higher pressures, and the ratio p_2/p_1 fell to 1.61. By again reducing the initial pressure to 250 mm., the ratio p_2/p_1 fell to 1.52, and the condensed products further increased. Lowering the pressure had therefore much the same influence upon the final result as increasing the cooling action of the walls of the containing vessel.

The results of these typical experiments are reproduced below :

	(a). Long cylinder.	(b). Large globe.	
p_1	701 mm.	685 mm.	448 mm.
p_2	1018 "	1187 "	724 "
p_2/p_1	1.45	1.73	1.61
Percentage composition of gaseous products.			
$\left\{ \begin{array}{l} \text{CO}_2 \text{} \\ \text{CO} \text{} \\ \text{C}_2\text{H}_2 \text{ ...} \\ \text{C}_2\text{H}_4 \text{ ...} \\ \text{CH}_4 \text{} \\ \text{H}_2 \text{} \end{array} \right.$	$\left. \begin{array}{l} 4.20 \\ 34.80 \\ 5.00 \\ 2.65 \\ 8.85 \\ 44.50 \end{array} \right\} 7.65$	$\left. \begin{array}{l} 3.40 \\ 36.10 \\ 0.15 \\ 7.25 \\ 53.05 \end{array} \right.$	$\left. \begin{array}{l} 4.00 \\ 31.10 \\ 2.25 \\ 6.85 \\ 52.80 \end{array} \right.$
	Units of	Units of	Units of
	C. H. O.	C. H. O.	C. H. O.
Original mixture ...	691 1041 354	678 1017 346	413 665 226
Final products	643 738 220	558 805 255	358 502 152
Difference	51 303 134	120 212 91	85 163 74
Percentage difference	7.6 29 37.8	18 20 27.5	19 24.5 32.8

The above results, showing as they do that water, unsaturated hydrocarbons, and aldehydes are prominently produced during the initial

stages of combustion in ordinary flames, whereas carbon is, comparatively speaking, a later product, are entirely in accordance with the views set forth in our previous paper. For if the successive stages in the combustion of ethane are correctly represented by the scheme



it is obvious that ethylene would arise at an early stage, for example, as the result of the thermal decomposition of ethyl alcohol, $\text{C}_2\text{H}_5\cdot\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$, and it is not difficult to explain the early formation of acetylene also, since acetylene is a prominent decomposition product of ethylene. Both steam and aldehydes would be formed in large quantities during the initial stages by the decomposition of hydroxylated molecules, but carbon would be a later product of the breaking down of acetaldehyde and unsaturated hydrocarbons. The incandescent carbon so liberated would rapidly react with steam, so that the longer the duration of the flame, the less the steam found in the final products.

(ii) *Experiments with a Mixture of Ethylene and Oxygen, $3\text{C}_2\text{H}_4 + 2\text{O}_2$.*

Similar striking differences in the relative proportions of the various products according to the rate of cooling were observed with this mixture, as in the foregoing experiments with ethane and oxygen, as follows:

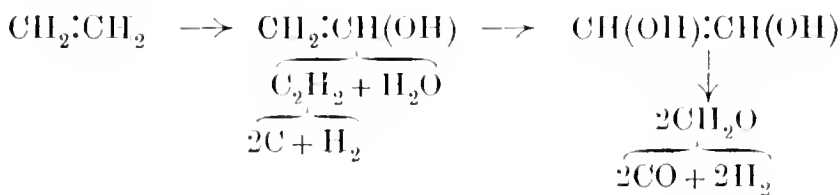
(a) When the shorter and narrower cylinder *C* was employed, the flame rapidly traversed the whole of the mixture. Some carbon separated, and much water and aldehydes were formed. The ratio p_2/p_1 was 1.407, and the gaseous products contained no less than 10 per cent. of acetylene, which was undoubtedly produced at a very early stage of the combustion process.

(b) With the longer and wider cylinder *B*, where the cooling would be somewhat less rapid, the flame ran down the tube in considerably less than a second. There was a sharp click when it reached the far end, but the vessel remained intact, and there was no evidence of detonation. More carbon separated than in the previous experiment, and the gaseous products contained much less acetylene, only 3.75 per cent. in fact. Much water condensed on cooling, and the rinsings gave a very strong aldehydic reaction; about 21 per cent. of the original oxygen appeared in the condensed products, as compared with 25 per cent. in the previous experiment, so that the somewhat less rapid

cooling had a distinct influence on the quantities of steam and aldehydes which survived the flame. The ratio p_2/p_1 was 1.44.

(c) The effect of retarded cooling was very marked in the experiments with the large globe *A*. There was a larger separation of carbon and a much less condensation of water than in the previous experiments, whilst the acetylene in the final products did not exceed 0.4 per cent. At the same time, practically the whole of the aldehydes were decomposed in the flame, for when Schiff's test was applied to the rinsings, no coloration appeared even after long standing. The ratio p_2/p_1 was now 1.78. Clearly, therefore, the longer duration of the flame had brought about the almost entire disappearance of acetylene and aldehydes, and had greatly facilitated the decomposition of the steam by incandescent carbon, so that the final products obtained were for the most part secondary in character.

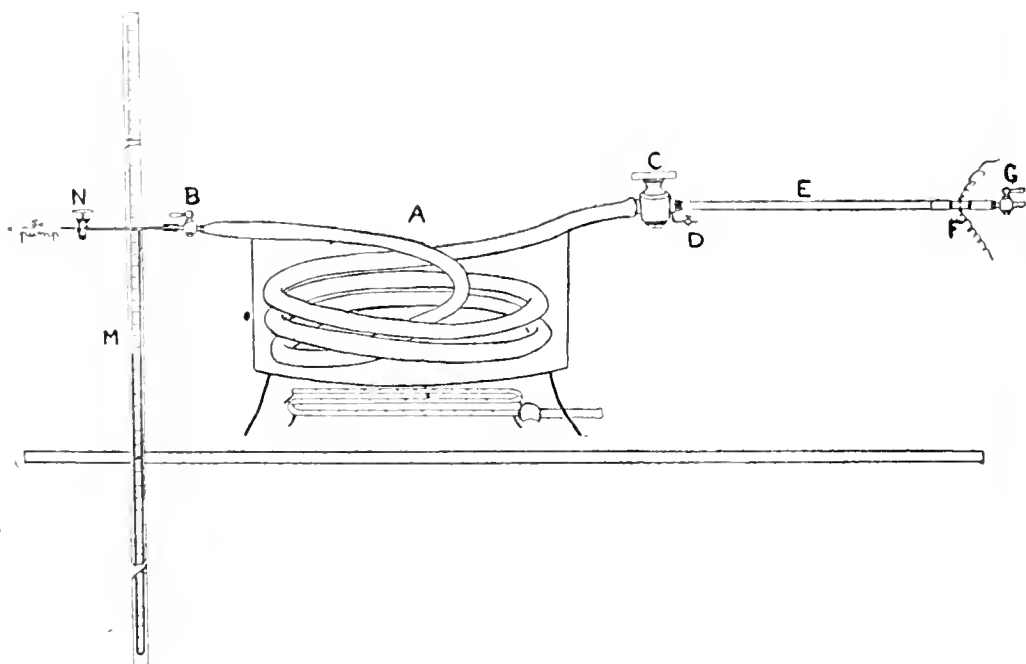
The results of these experiments, which are tabulated below, are in complete harmony with our theory of combustion, as will be seen from the following scheme :



	(a). Short, narrow cylinder, <i>C</i> .	(b). Long cylinder, <i>B</i> .	(c). Large globe, <i>A</i> .
p_1	753 mm.	730 mm.	756 mm.
p_2	1080 "	1053 "	1356 "
p_2/p_1	1.407	1.44	1.78
Percentage composition of gaseous products.	CO ₂	2.50	0.50
	CO	40.10	41.45
	C ₂ H ₂ ...	3.75	} 0.40
	C ₂ H ₄ ...	1.25	
	CH ₄	5.20	2.90
	H ₂	47.20	51.75
	O ₂	nil	nil
<hr/>			
	Units of	Units of	Units of
	C. H. O.	C. H. O.	C. H. O.
Original mixture ...	879 879 310	856 856 302	883 883 310
Gaseous products ...	737 703 233	608 676 237	611 819 284
Difference	142 176 77	248 180 65	272 64 26
Percentage difference	16 20 25	29 21 21	31 7.2 8.4

II. *Experiments on the Detonation of Mixtures corresponding to $C_2H_6 + O_2$ and $C_4H_{10} + 2O_2$ respectively.*

Detonation is not readily set up in an equimolecular mixture of ethane and oxygen, and to ensure success we found it necessary to work at fairly high pressures with a stout leaden coil of rather large diameter, and also to start the explosion wave in a special firing-piece containing electrolytic gas under high pressure. The arrangement of our apparatus is shown in the accompanying sketch.



The lead coil, *A*, was 20 feet long, 31 mm. external and 26 mm. internal diameter, with a capacity of 3100 c.c. It was set in position in a large water-bath, so that its contents could be heated to the boiling point of water just before being fired or, after the explosion, rapidly cooled again to the ordinary temperature by water from the mains. One end of the coil was closed by a gun-metal cock, *B*, such as is used in connection with high pressure steam gauges. Through this cock, connexion could be established with the capillary manometer, *M*, and also through the stopcock, *N*, with a mercurial- or water-pump as occasion demanded.

The other end of the coil terminated in a large steel tap, *C*, of wide bore, provided with a small side-tap, *D*, on the side remote from the coil. The tap *C* communicated with the "firing-piece," *E*, composed of lead tubing 1.0 metre long and 12 mm. in diameter, provided with suitable firing wires fused in through a stout glass piece, *F*. The other

end of the firing-piece was closed by the gun-metal cock, *G*, similar in design to *B*. The capacity of the firing-piece was 120 c.c., and it will be seen that by closing the steel tap *C*, the firing-piece could be filled with electrolytic gas at any desired pressure, after the coil itself had been filled with the experimental mixture. The small side-tap, *D*, allowed of the gas previously in the firing-piece being swept out by the electrolytic gas.

After the apparatus had been set up, it was thoroughly tested as follows: (1) it was completely exhausted and allowed to stand vacuum for two days in connection with the manometer, but no air entered; (2) oxygen was maintained in the coil and firing-piece at 4 atmospheres pressure for several hours without any appreciable escape; (3) finally, the coil and firing-piece were filled at atmospheric temperature with an equimolecular mixture of ethylene at a pressure of 680 mm. On firing the mixture, detonation was set up, but there was no escape of gas, and except for a slight increase in the volume of the coil (about 35 c.c.), due to the force of the explosion, the apparatus remained perfectly intact. After allowing for this slight increase in volume, the "corrected" final pressure of the cold products was 1346 mm., so that $p_2/p_1 = 1.98$. Since the mixture $C_2H_4 + O_2$ is known to yield carbon monoxide and hydrogen on detonation, $C_2H_4 + O_2 = [2CH_2O] = 2CO + 2H_2$, the ratio 1.98 showed that the apparatus could be relied on to resist successfully the shock of detonation without any outleakage of the gaseous products.

(a) *With the Mixture $C_2H_6 + O_2$.*

The question at issue was, will this mixture on detonation exhibit a preferential combustion of carbon, $C_2H_6 + O_2 = 2CO + 3H_2$, or will the course of events be essentially the same as in ordinary inflammation?

Three experiments were made, the first two with a mixture containing $C_2H_6 = 50.25$ and $O_2 = 49.75$ per cent., the third with one containing $C_2H_6 = 50.1$ and $O_2 = 49.9$ per cent. respectively, as follows:

(1) The coil was filled at 17° and 906 mm. with the experimental mixture and its temperature raised to 98° . Meanwhile the firing-piece was charged with electrolytic gas at $2\frac{1}{2}$ atmospheres' pressure. The connecting tap, *C*, was then opened, and five seconds later the electrolytic gas was fired. A heavy sound indicated the setting up of detonation in the electrolytic gas, and at the same instant a sharp metallic click at the far end of the coil showed that the explosion-wave had been propagated through the mixture of ethane and oxygen in the coil.

The hot water surrounding the coil was rapidly discharged through

three large syphons, and immediately afterwards the bath was filled up with cold water from the mains, so that within a minute of the explosion the contents of the coil were cooled down to the ordinary temperature. The tap *B* communicating with the manometer was opened, and the pressure read about two minutes later. The mercury in the manometer kept perfectly steady for half an hour, showing that all joints and connections had remained quite tight. So violent had been the explosion that the volume of the coil had increased from 3100 to 3300 c.c., and careful measurement with a pair of callipers showed that its diameter had increased slightly throughout its whole length. Allowing for the increase in the volume of the coil, and for the fact that the products now filled both coil and firing-piece, the "corrected" pressure of the cold product was 1700 mm. or $p_2/p_1 = 1.86$.

(2) The experiment was repeated with the same coil, the initial pressure being 1180 mm. The firing-piece was charged up to 3 atmospheres with electrolytic gas. The explosion was very violent, the coil being visibly enlarged, its volume increasing from 3300 to 3900 c.c., but otherwise it remained quite intact. Making due allowance for this increase in volume, and for the fact that the products filled both coil and firing-piece, the "corrected" pressure of the cold products was 2240 mm., so that $p_2/p_1 = 1.90$.

On subsequent exhaustion, the apparatus sustained the vacuum perfectly for sixteen hours. An examination of the coil showed how violent had been the explosion. The external diameter at the end nearest the connecting tap *C*, where the explosion-wave entered the coil, had remained 31 mm., but 20 cm. along the coil it had already become 33.5 mm., and for the greater part of its length it was 34.5 mm. The far end nearest the cock *B*, the coil had become pear-shaped, the diameter at the widest part being no less than 44 mm. So seriously had the coil been strained that it was deemed unsafe to use it further, and a new one of similar internal dimensions, but with somewhat stronger walls, was installed in its place.

(3) The new coil had a capacity of 3080 c.c. The original mixture was charged in at a pressure of 987 mm., and the firing-piece was filled with electrolytic gas at $2\frac{1}{2}$ atmospheres. The procedure was the same as in the two previous experiments. The coil was expanded from 3080 to 3280 c.c. by the explosion. The corrected final pressure of the cold products was 1802 mm., so that $p_2/p_1 = 1.83$.

(4) This experiment was designed to prove the instantaneous character of the explosion. It will be remembered that when the mixture $C_2H_6 + O_2$ was inflamed in the long glass cylinder under ordinary conditions, the flame travelled quite slowly through the mixture at a rate of half a metre per second. At this rate, it would have taken about twelve seconds to travel down the coil. The contrast between

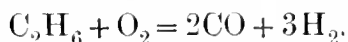
this state of things and detonation is evident from the following description. After the coil had been filled with the mixture at 1000 mm. pressure, the pump and manometer connections were removed, and a short, stout glass test-tube was firmly attached by means of pressure tubing to the cock *B*. The cock was then opened, and the contents of the coil fired in the usual manner. Instantly there was a deafening report, the test-tube being reduced to fine powder. A black smoke was projected from the coil, an indication of the liberation of carbon during the explosion.

The instantaneous character of the explosion, which was certainly propagated through the gaseous mixture with very great velocity, and its violence, as demonstrated by the enlargement of the coil throughout its whole length, leave little room for doubt that the conditions of the above experiments were those of "detonation" and not of ordinary "inflammation."

The results of the above experiments are tabulated below :

	1.	2.	3.
p_1	906 mm.	1180 mm.	981 mm.
p_2	1700 "	2240 "	1802 "
p_2/p_1	1.86	1.90	1.83
Percentage composition of gaseous products.			
$\left\{ \begin{array}{l} \text{CO}_2 \text{} \\ \text{CO} \text{} \\ \text{C}_2\text{H}_2 \text{ ...} \\ \text{C}_2\text{H}_4 \text{ ...} \\ \text{CH}_4 \text{} \\ \text{H}_2 \text{} \end{array} \right.$	$\left\{ \begin{array}{l} 1.65 \\ 39.00 \\ 1.20 \\ 0.50 \\ 6.65 \\ 51.00 \end{array} \right.$	$\left\{ \begin{array}{l} 1.80 \\ 39.10 \\ 0.90 \\ 0.50 \\ 7.70 \\ 50.00 \end{array} \right.$	$\left. \begin{array}{l} 2.2 \\ 38.1 \\ 2.5 \\ 8.1 \\ 49.1 \end{array} \right\}$
	Units of	Units of	Units of
	C. H. O.	C. H. O.	C. H. O.
In original mixture..	910 1365 451	1186 1779 587	986 1479 491
In gaseous products.	862 1131 359	1151 1507 488	962 1237 383
Difference	48 234 92	35 272 99	24 242 108
Percentage difference	5.3 17 20	3 15 17	2.5 17 22

Considering now the main question at issue in light of the above results, it is clear that they are decisive against the theory that in "detonation" a preferential combustion occurs, for example,



On the other hand, the great similarity between these results and those obtained when the same original mixture was "inflamed" under

ordinary conditions, warrants the view that the mechanism of combustion is essentially the same in both "*detonation*" and "*inflammation*." Indeed, it seems impossible to explain the appearance of as much as 20 per cent. of the original oxygen among the condensed products, and the presence of from 6.5 to 8.0 per cent. of methane in the gaseous products, in the above experiments, except on the assumption that in "*detonation*," as in ordinary flames, hydroxylated molecules are initially produced. The difference between the true phenomena is probably mainly one of temperature. At the much higher temperature of the explosion wave, the reduction of steam by any carbon liberated is greatly accelerated, so that less of both these products survive than is the case with ordinary flames.

The great stability of methane at such high temperatures is strikingly demonstrated by the above results. Indeed, it would seem as though the rate at which methane is decomposed in the flame is much slower than that at which the liberated carbon reduces steam. We surmise that with gradually increasing initial pressures the methane would be more and more decomposed in the flame, and in consequence the steam more and more decomposed by the carbon liberated, until, at some doubtless very high pressure, the final products would consist mainly, if not entirely, of carbon monoxide and hydrogen, as though preferential combustion of carbon had occurred. This is a problem which one of us is now investigating with an apparatus especially designed for high pressure work.

(b) *With the Mixture $C_4H_{10} + 2O_2$.*

It was deemed advisable to make at least one experiment with a higher paraffin, and for this purpose *n*-butane was selected. The original mixture contained $C_4H_{10} = 34.0$ and $O_2 = 66.0$ per cent. At first we attempted to set up detonation in this mixture at atmospheric pressure, with the firing piece charged with electrolytic gas up to 3 atmospheres, but without success. The explosion wave was, of course, set up in the electrolytic gas, but died out shortly after entering the coil.

In the one successful experiment the coil was filled with the experimental mixture at 16° and 929 mm., and the firing piece, with electrolytic gas under 3 atmospheres. The procedure was the same as in previous experiments. On firing, the explosion wave was propagated through the whole mixture, and the violence of the explosion caused an increase in the volume of the coil from 3225 to 3450 c.c. Allowing for this expansion, and the fact that the products filled both the coil and firing piece, the corrected pressure of the cold products was 2170 mm., so that $p_2/p_1 = 2.33$. The results of this experiment,

which are given below, entirely confirmed those obtained with ethane. It will be seen that the gaseous products contained no less than 6·2 per cent. of methane, and that as much as 15 per cent. of the original oxygen appeared in the condensed products.

$$p_1 = 929 \text{ mm.}, p_2 = 2170 \text{ mm.}, p_2/p_1 = 2\cdot33.$$

Gaseous products.		per cent.		Units of		
				C.	H.	O.
$\left\{ \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \end{array} \right\}$	CO_2	= 1·70.	Original mixture	1264	1580	613
	CO	= 44·6.		1221	1320	521
	C_2H_2	= 1·9.	Difference	43	260	92
	C_2H_4		Percentage difference...	3·5	16·5	15
$\left\{ \begin{array}{l} \text{CH}_4 \\ \text{H}_2 \end{array} \right\}$	CH_4	= 6·2.				
	H_2	= 45·6.				

In conclusion, we desire again to acknowledge our indebtedness to the Government Grant Committee of the Royal Society for grants towards the expenses of this research.

UNIVERSITY, MANCHESTER.

CLXIV.—*Derivatives of Polyvalent Iodine. The Action of Chlorine on Organic Iodo-derivatives, including the Sulphonium and Tetra-substituted Ammonium Iodides.*

By EMIL ALPHONSE WERNER.

SINCE the original preparation of *o*-iodosobenzoic acid by V. Meyer and Wachter in 1892 (*Ber.*, **25**, 2632), and the subsequent discovery of the remarkable iodonium compounds two years later by V. Meyer and Hartmann (*Ber.*, **27**, 426), numerous additions to our knowledge of these interesting iodine derivatives have been made, particularly by Willgerodt and his pupils.

As far back as 1886, Willgerodt (*J. pr. Chem.*, [ii], **33**, 154) showed that chlorine under ordinary conditions does not displace the iodine in iodobenzene, but forms the addition compound $\text{C}_6\text{H}_5\cdot\text{ICl}_2$, from which iodosobenzene and diphenyliodonium hydroxide may be prepared; indeed, this compound may be regarded as the parent substance from which all these basic compounds of tervalent iodine are derived. The marked difference in the behaviour of iodine towards chlorine, when the former is in union with the phenyl or methyl group, for instance, is very remarkable, and suggests the question, “is union with a closed carbon chain an essential condition for this behaviour of the iodine

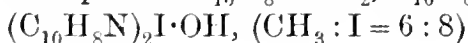
atom." Willgerodt and his co-workers have shown that the presence of different negative elements or radicles, such as Br, Cl, NO_2 , SO_3H , $\text{CO}\cdot\text{C}_6\text{H}_5$, in the benzene nucleus does not materially affect the power of the iodine of uniting directly with chlorine, and this is also true of the presence of the aliphatic hydrocarbon radicles, such as CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} , the corresponding iodoso- and iodonium-derivatives being obtainable in most cases from the dichloro-addition compounds (Willgerodt, *Ber.*, 1893, **26**, 1532, 1802; Willgerodt and Brandt, *J. pr. Chem.*, 1904, [ii], **69**, 433; Willgerodt and Rampocher, *Ber.*, 1901, **34**, 3666; Willgerodt and Dammann, *Ber.*, 1901, **34**, 3678).

In the case of iodomesitylene, both the dichloride, $\text{C}_6\text{H}_2(\text{CH}_3)_3\cdot\text{ICl}_2$, and the iodoso-derivative, $\text{C}_6\text{H}_2(\text{CH}_3)_3\cdot\text{IO}$, are very unstable (Willgerodt and Roggatz, *J. pr. Chem.*, 1900, [ii], **61**, 423).

More recently it has been shown that *m*-di-iodobenzene can unite with chlorine in two stages to form the compounds $\text{C}_6\text{H}_4\text{I}\cdot\text{ICl}_2$ and $\text{C}_6\text{H}_4(\text{ICl}_2)_2$, from which the basic oxides $\text{C}_6\text{H}_4\text{I}\cdot\text{IO}$ and $\text{C}_6\text{H}_4(\text{IO})_2$ respectively have been prepared (Willgerodt and Desaga, *Ber.*, 1904, **37**, 1301). whilst from 3:4-di-iodotoluene only the compound $\text{C}_6\text{H}_3\text{MeI}\cdot\text{ICl}_2$ was obtained on chlorination, and the corresponding iodoso-derivative could not be isolated (Willgerodt and Simonis, *Ber.*, 1906, **39**, 269). These results show that the presence of a methyl group in the benzene nucleus can destroy the tervalent power of one of the iodine atoms, whilst the presence of three methyl groups is capable of seriously impairing the tervalent power of even the single iodine atom.

On the other hand, McCrae (*Trans.*, 1898, **73**, 691) easily obtained a dibromiodosotoluene from the compound $\text{C}_7\text{H}_5\text{Br}_2\cdot\text{ICl}_2$, prepared from 3:5:2-dibromiodotoluene, and also a tribromiodosobenzene from the compound $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{ICl}_2$, prepared from 1:3:5:2-tribromiodobenzene; here the presence of two and three atoms respectively of bromine does not sensibly interfere with the combining power of the iodine, but again Willgerodt and Ernst (*Ber.*, 1901, **34**, 3406), from *s*-di-iodonitrobenzene, could only obtain the compound $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{ICl}_2$, and the corresponding iodoso- and iodoxy-derivatives; in this case, the negative NO_2 group has destroyed the tervalence of one of the iodine atoms, just as the positive CH_3 group has done in 3:4-di-iodotoluene.

All the published work up to the present, with a single exception, which will be referred to presently, has been restricted to the study of the immediate derivatives of benzene, excepting, perhaps, iodonaphthalene, which forms the compound, $\text{C}_{10}\text{H}_7\text{I}\cdot\text{Cl}_2$, and iodosonaphthalene, $\text{C}_{10}\text{H}_7\cdot\text{IO}$ (Willgerodt, *Ber.*, 1904, **37**, 590), and iodomethylquinoline, from which the compounds $\text{C}_{10}\text{H}_8\text{N}\cdot\text{ICl}_2$, $\text{C}_{10}\text{H}_8\text{N}\cdot\text{IO}$, and



have been prepared (Willgerodt and Frischmuth, *Ber.*, 1905, 38, 1805).

The fact that the iodine atom when in union with the benzene and the closely related naphthalene and quinoline rings is capable of exhibiting a property unassociated with the element in its union with carbon in an open chain has now been definitely recognised. The questions which naturally arise from a consideration of this peculiar difference, in addition to the one already mentioned are:

1. Has the mass of the radicle in union with iodine any influence on the occurrence of this property.

2. What changes in the carbon ring will destroy the property, or leave it unaltered.

3. Is the property of tervalence, accompanied by the production of basic bodies, peculiar to the union of iodine with carbon.

With these ideas in mind, I have made a number of experiments on the action of chlorine on different organic iodo-derivatives.

The following open chain compounds, when subjected to the action of chlorine in solution in chloroform or carbon tetrachloride, are changed into the corresponding chlorides with separation of the iodine, namely, *sec.*-butyl-, *tert.*-butyl-, *iso*amyl-, and *n*-hexyl-iodides, acetyl, and propionyl iodides. In this series, we have the combinations $-\text{CH}_2\text{I}$, $=\text{CHI}$ and $\equiv\text{CI}$, the groups $\text{C}_5\text{H}_{11}-$ and $\text{C}_6\text{H}_{13}-$, and the negative acyl radicles; the results prove at once that, all other conditions being equal, neither the nature of the radicle, whether positive or negative, nor its mass in the case of an open chain compound, has any effect on the valency of the iodine.

In these experiments the temperature was never below -8° . While the work described in the present paper was in progress, an interesting communication by Thiele and Peter (*Ber.*, 1905, 38, 2842) appeared; these chemists have obtained methyl iodochloride by the action of chlorine on a solution of methyl iodide in carbon tetrachloride and light petroleum cooled by a carbon dioxide-ether mixture (presumably about -75°); the compound melts at -28° and decomposes into methyl chloride and iodine monochloride.

The iodochlorides prepared from the higher homologues are much less stable, thus *sec.*-butyl iodochloride decomposes at -100° , and even below this temperature chlorine liberates the iodine from *tert.*-butyl iodide in the ordinary way. These experiments of Thiele and Peter show what a wide gap, in the direction of lowering of temperature, must be overcome before the iodine atom in union with an open carbon chain can exert even in a feeble degree the tervalent power which is so readily brought into play when in union with the carbon ring of benzene.

It has yet to be shown that the dichloride, $\text{CH}_3\cdot\text{ICl}_2$, is not a

molecular compound of the composition, $\text{CH}_3\text{Cl}\cdot\text{ICl}$, corresponding to the class of derivatives produced from iodine chloride to be later described.

It appears evident from the work of Willgerodt and his pupils that almost any mono- or di-substituted derivatives of iodobenzene can unite with chlorine to form iodochlorides, from which iodoso-, iodoxy-, and iodonium compounds may be prepared; I have made experiments with a few benzene derivatives which do not appear to have been hitherto examined, and in each case derivatives of tervalent iodine were readily formed.

p-Iodoacetophenone gives the *dichloride*, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{ICl}_2$, and the *iodoso*-compound, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{IO}$; *p*-iodoacetanilide gives the *dichloride*, $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{ICl}_2$, which undergoes partial fusion at $110\text{--}112^\circ$ with evolution of chlorine (see experimental part); the *iodoso*-derivative is a buff-coloured powder having a strong odour of iodoform.

Di-iododiphenyl gives a *tetrachloride*, from which the *iodoso*-derivative and the *tetra-acetate*, $(\text{C}_6\text{H}_4)_2\text{I}_2(\text{OAc})_4$, have been obtained.

From the three *o*-, *m*-, and *p*-iodonitrobenzenes, the corresponding iodochlorides, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{ICl}_2$ were prepared, when it was found that these substances had already been studied by Willgerodt (*Ber.*, 1893, 26, 1532, 1802); the ortho-compound melts at 96° , the meta- at 97° (Willgerodt gives $100\text{--}102^\circ$) and the para- at 170° (not stated by Willgerodt); in each case there is brisk evolution of chlorine as the substance melts.

I have noticed, in connection with the *iodoso*-derivatives produced from these isomeric chlorides, that the *p*-compound possesses distinctly feebler basic power than the *o*- and *m*-compounds; this is rather remarkable, bearing in mind that the negative NO_2 group is furthest removed from the iodine in the former.

Professor Willgerodt has expressed a desire to reserve for himself the study of the *iodoso*- and iodonium derivatives of benzene and its homologues (*Ber.*, 1900, 33, 853), so that I have made no further experiments in this direction.

In seeking to obtain information as to the effects produced by changes in the carbon ring, I was naturally led to examine the behaviour of the iodo-derivatives of thiophen. The results of my experiments on α -iodothiophen ($\text{S}:\text{I}=1:2$) and di-iodothiophen show that the presence of the sulphur in the carbon ring prevents the iodine from forming addition compounds with chlorine, both substances being decomposed similarly to the aliphatic iodides.

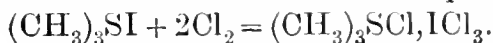
Strangely enough, the presence of the imino-group does not produce the same effect; tetraiodopyrrole, when subjected to the action of chlorine in glacial acetic acid or chloroform solution, yields the addition

compounds $C_4HNI_4Cl_4$ and $C_4HNI_3Cl_3$ without the liberation of even a trace of iodine. Although these compounds have only been superficially examined so far, it seems likely that only two out of the four iodine atoms have been able to exert their tervalence; the first compound is probably $C_4HNI_2(ICl_2)_2$. In connection with the pyrrole compound, it is interesting to note that Thiele and Peter (*Ber.*, 1905, 38, 2842), by the action of chlorine on chloriodofumaric acid, have obtained an iodosochloride, to which they attribute the constitution $\begin{array}{c} CCl \cdot CO \\ || \\ CH \cdot ICl \end{array} > O$; in this case, the tervalence of the iodine is distributed between carbon, chlorine, and oxygen, in which respect this compound differs from all the other organic derivatives of polyvalent iodine hitherto described. The existence of such a compound is of no help in predicting the probable behaviour of iodine in a ring compound such as furfuran, the oxygen analogue of thiophen. The difficulty of obtaining iodo-derivatives of this compound has debarred me from securing any experimental evidence on this interesting point.

As regards the behaviour of iodine in union with elements other than carbon, we have undoubted evidence of its polyvalent character in such compounds as iodine trichloride, iodic acid, and periodic acid and the many derivatives of the latter; for instance, Blomstrand (*Zeit. anorg. Chem.*, 1892, 1, 10) explains the constitution of the several complex molybdoperiodates examined by him on the assumption that the iodine is heptavalent, the constitution of periodic acid being $O:I(OH)_5$. All these compounds of iodine possess the normal properties usually connected with the presence of a negative element; thus we know of no basic derivatives of iodine outside the class of compounds prepared by V. Meyer and by Willgerodt.

In the hope of obtaining derivatives of polyvalent iodine in which the element is in direct union with sulphur and nitrogen respectively, the action of chlorine on the sulphonium and tetra-substituted ammonium iodides has been examined; in each case, chlorine additive compounds were formed, which, on preliminary examination, appeared to belong to the type of derivatives sought for, but no iodine bases could be produced from them.

When chlorine is passed into an ice-cold solution of trimethylsulphonium iodide in glacial acetic acid containing about 8 per cent. of carbon tetrachloride, a momentary liberation of iodine takes place, quickly followed by the separation of a bright chrome-yellow *tetrachloro*-derivative. This substance, which has the composition $C_3H_9Cl_4IS$, is produced in accordance with the equation



This, it might be expected, would involve the liberation of all the iodine before the trichloride and the subsequent addition compound

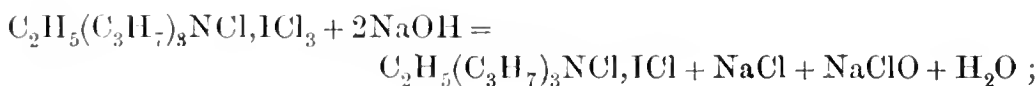
would be formed; such, however, is apparently not the case; the latter, when once formed, is produced almost as rapidly as the iodine is liberated, with the result that when the reaction is well in progress the proportion of free iodine in the liquid at any time is always comparatively small.

In the case of the tetra-substituted ammonium iodides, the reactions take place just as readily with formation of addition compounds of the same type, and in some instances the products are almost as easily formed from these iodides, using an aqueous solution.

The following *compounds*, the properties of which are described in the experimental part of the paper, have been prepared and partially studied: $(\text{CH}_3)_3\text{SCI}, \text{ICl}_3$, $(\text{C}_2\text{H}_5)_3\text{SCI}, \text{ICl}_3$, $\text{C}_2\text{H}_5(\text{C}_3\text{H}_7)_3\text{NCl}, \text{ICl}_3$, $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{C}_2\text{H}_5\text{NCl}, \text{ICl}_3$, $\text{C}_5\text{H}_5\text{N}, \text{C}_2\text{H}_5\text{Cl}, \text{ICl}_3$.

These compounds are quite stable at the ordinary temperature; when heated, chlorine is gradually evolved until two atomic proportions have been given off, when the much more stable iodochlorides remain, such as $(\text{CH}_3)_3\text{SCI}, \text{ICl}$ (m. p. 103°), $\text{C}_2\text{H}_5(\text{C}_3\text{H}_7)_3\text{NCl}, \text{ICl}$ (m. p. 94°), and $\text{C}_5\text{H}_5\text{N}, \text{C}_2\text{H}_5\text{Cl}, \text{ICl}$ (m. p. 35°); these can be obtained in golden-yellow or orange crystals from solutions in alcohol, glacial acetic acid, or hydrochloric acid. They are particularly stable in presence of the last solvent; the compound $\text{C}_2\text{H}_5(\text{C}_3\text{H}_7)_3\text{NCl}, \text{ICl}$, when heated to 160° with a 10 per cent. hydrochloric acid solution, crystallises, on cooling, unchanged; in the dry state the substance does not decompose until heated to 185° .

These compounds are also formed when the original chlorine derivatives are triturated carefully with a solution of sodium hydroxide in accordance with the equation, for instance:



excess of alkali effects further decomposition with removal of both iodine and chlorine, the former chiefly as iodate, but its action has not been fully investigated up to the present.

A third method by which these iodochlorides may be prepared consists in acting directly on the sulphonium or substituted ammonium chlorides with a solution of Schützenberger's compound, ICl, HCl ; in this way the following *compounds* were prepared: $(\text{C}_3\text{H}_7)_3\text{HNCl}, \text{ICl}$ (m. p. 42°), $(\text{C}_3\text{H}_7)_2\text{H}_2\text{NCl}, \text{ICl}$ (m. p. 45°), $(\text{CH}_3)_4\text{NCl}, \text{ICl}$ (m. p. 217°), $(\text{C}_2\text{H}_5)_4\text{NCl}, \text{ICl}$ (m. p. 98°), $\text{C}_5\text{H}_5\text{N}, \text{HCl}, \text{ICl}$ (m. p. 175°), $(\text{C}_2\text{H}_5)_3\text{SCI}, \text{ICl}$, a viscid, orange-red liquid.

E. Ostermeyer (*Chem. Centr.*, 1884, 15, 937), by the action of Schützenberger's compound on quinoline and on pyridine, has already

obtained derivatives of this kind, the composition of which he represents by the formulæ C_9H_7N, ICl, HCl (m. p. 118°) and

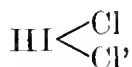


(m. p. 178°), that is, as hydrochlorides of the bases C_9H_7N, ICl and C_5H_5N, ICl respectively.

Whether these two classes of compounds here described and represented by the types C_5H_5N, C_2H_5Cl, ICl_3 and C_5H_5N, C_2H_5Cl, ICl are to be regarded as derivatives of polyvalent iodine is open to question. If one is to judge from the conclusions arrived at, as a result of the investigations during recent years, on the constitution of complex compounds, there appears to be a tendency to put aside the old notion of molecular compounds and to explain the constitution of most of these substances by attributing an increased valency to one or other of the elements concerned; this is particularly the case in connection with the evidence which is brought forward in support of the basic properties of oxygen.

Considering their methods of formation and the properties of these compounds, and particularly the ease with which the iodine is removed by treatment with caustic alkali, I am inclined to regard them simply as molecular compounds containing iodine trichloride and iodine monochloride respectively, in union with the different basic chlorides. On the other hand, it may be urged that, whilst they are quite distinct from the iodoso-chlorides derived from benzene and its allied ring compounds, they are, nevertheless, derivatives of polyvalent iodine in which the combining power of that element is greatly weakened by the particular conditions of constitution, such as, for instance, the predominance of negative elements in the immediate surrounding of the iodine atom.

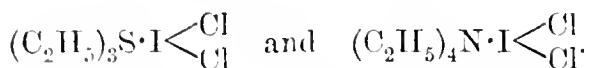
If Schützenberger's compound, ICl, HCl * (*Compt. rend.*, 1877, 84, 389), be considered as a derivative of trivalent iodine, then its constitution may obviously be written thus:



in which case the second class of iodochlorides might be considered to

* This compound, which is quite as stable as iodinetrichloride, may be conveniently obtained in solution as follows: 50 grams of sodium nitrite dissolved in 120 c.c. of water are slowly added to 50 grams of potassium iodide dissolved in 200 c.c. of strong hydrochloric acid; the liquid is boiled under a reflux condenser until all brown fumes cease to be evolved (Ostermeyer, *loc. cit.*). Ether extracts the compound from this solution and, on evaporation, leaves it as an orange-red liquid which is quite stable at the ordinary temperature if protected from the light.

be derived from this substance by the substitution of hydrogen by positive sulphur or nitrogen radicles, such as



Much evidence is necessary, however, before such a view of the constitution of these compounds can be definitely put forward, and in the absence of further evidence I prefer to consider these derivatives simply as molecular compounds of the types already mentioned.

EXPERIMENTAL.

Action of Chlorine on p-Iodoacetophenone.

When chlorine is passed into a cold 10 per cent. chloroform solution of this substance, there is no separation of iodine, and the *dichloride* is soon obtained in very pale yellow, microscopic needles which melt at 90—91°. These were washed with chloroform and dried by pressure between bibulous paper and exposure to the air until the odour of chloroform had disappeared. The yield was 85 per cent. of the theoretical.

Analysis gave Cl = 21.63.

$\text{C}_8\text{H}_7\text{OCl}_2\text{I}$ requires Cl = 22.39 per cent.

Unlike most iodochlorides, this compound on heating only suffers partial loss of chlorine, with formation of probably a new substituted derivative.

The following observations were made in an experiment performed with 2 grams of the dry substance.

At 58° slight evolution of chlorine commenced, at 90—91° fusion set in, quickly followed by a sudden, brisk effervescence at 98°, chlorine and some hydrogen chloride being evolved; the temperature was raised to 125° without any further evolution of gas. The residue, when crystallised from benzene, melted at 116—117°, the melting point of *p*-iodoacetophenone being 84°. (Klingel, who first prepared this compound, gives its melting point as 78°.)

When the iodochloride from *o*-iodonitrobenzene was heated, evolution of chlorine commenced at the outset (16°) and continued slowly up to 96°, at which temperature the substance melts with rapid evolution of chlorine.

In an experiment using 2 grams, Cl evolved = 21.75.

$\text{C}_6\text{H}_4\text{O}_2\text{NCl}_2\text{I}$ requires Cl = 22.18 per cent.

Crystallised from chloroform, the residue melted at 49°, which is the melting point of *o*-iodonitrobenzene. In this case, therefore, the action

of heat is simply to expel the chlorine, and this appears to be the general result observed so far by Willgerodt with the various iodo-chlorides which he has prepared.

p-Iodosoacetophenone, $\text{CH}_3\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{IO}$, is a white powder melting at $101\text{--}102^\circ$, having a very pleasant odour and easily prepared by the action of sodium hydroxide solution on the iodochloride.

0.248 gave 0.1194 iodine. $\text{I} = 48.14$.

$\text{C}_8\text{H}_7\text{O}_2\text{I}$ requires $\text{I} = 48.47$ per cent.

Its basic power is very feeble, due to the presence of the acetyl group.

Action of Chlorine on p-Iodoacetanilide.

When chlorine is passed into a 5 per cent. cold chloroform solution of this substance, no iodine is set free, and the *acetanilide-p-iododichloride* quickly separates as a pale orange-yellow, microcrystalline powder. The yield is nearly theoretical, as the compound is almost insoluble in chloroform.

Analysis gave $\text{Cl} = 21.23$.

$\text{C}_8\text{H}_5\text{ONCl}_2\text{I}$ requires $\text{Cl} = 21.38$ per cent.

The following points have been observed in the action of heat on this iodochloride, using 2 grams of the substance. At 95° evolution of chlorine commenced, at 112° there was sudden copious evolution of chlorine and partial fusion; as the heating was continued the liquid became dark orange-red, and there was no further evolution of chlorine up to 130° , when the heating was stopped. From the alcoholic solution of the residue, two distinct sets of crystals were obtained: (a) stout, lustrous prisms melting at 144° , and (b) thin, feathery crystals melting at 117° ; the original iodoacetanilide melts at 183° . In this case again the action of heat on the iodochloride has not followed the usual lines, some substitution products evidently being formed.

The *iodoso*-derivative, $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{IO}$, was prepared by acting on the chloride with sodium hydroxide; it is a buff powder having a strong odour resembling that of iodoform, and easily yields a crystalline acetate.

Action of Chlorine on Di-iododiphenyl.

The di-iododiphenyl (m. p. 169°) was prepared from benzidine by the aid of the diazo-reaction in the usual way; it was obtained in yellowish-brown scales from chloroform solution.

When chlorine was passed into a 10 per cent. chloroform solution,

cooled to 0° , no iodine was liberated, and the *di-iodotetrachloride* separated as a reddish-brown powder.

Analysis gave $\text{Cl} = 25.62$.

$\text{C}_{12}\text{H}_8\text{Cl}_4\text{I}_2$ requires $\text{Cl} = 25.91$ per cent.

The compound is unstable, and both chlorine and hydrogen chloride are slowly evolved on standing.

The *iodoso*-derivative melting at 127° was obtained as a chocolate-brown powder by the action of sodium hydroxide on the freshly-prepared iodochloride; the compound itself was not analysed, but the *acetate* was prepared by dissolving the oxide in hot glacial acetic acid and evaporating to dryness. It was purified by crystallisation from hot benzene, from which it separates in almost colourless, minute crystals melting at 203° .

0.182 gave 0.138 AgI. $\text{I} = 40.09$.

$\text{C}_{20}\text{H}_{20}\text{O}_8\text{I}_4$ requires $\text{I} = 39.56$ per cent.

This tetra-acetate decomposes with explosive violence when heated rapidly above its melting point.

I have not further examined any of these benzene derivatives, my immediate object being to ascertain whether these iodo-derivatives were capable or not of forming additive compounds with chlorine. As regards the action of heat on the iodochlorides, I hope to examine this change more fully in the near future.

Action of Chlorine on Tetraiodopyrrole, $\begin{array}{c} \text{Cl}:\text{Cl} \\ | \\ \text{Cl}:\text{Cl} \end{array} > \text{NH}.$

When chlorine is passed into a cold saturated solution of iodo-pyrrole in chloroform (this solution does not contain more than 3 per cent. of the iodo-compound) there is no separation of iodine; the liquid assumes a transitory red colour which quickly changes to golden-yellow. The addition compound remains in solution, but may be precipitated to some extent as a bright yellow powder by adding a large volume of light petroleum; the yield, however, is very small.

The following method of preparation has been found most suitable up to the present, although the yield is still poor.

Chlorine is rapidly passed into a saturated solution of the iodo-pyrrole in glacial acetic acid heated to about 25° ; when the chlorine is in excess the liquid is poured into about ten times its volume of ice-cold water, the addition compound is precipitated and quickly separated by the aid of the pump. After washing with light petroleum it is dried by pressure and exposure to dry air.

The freshly-prepared *compound* gave, on analysis, $\text{Cl} = 19.48$.

$\text{C}_4\text{HNCI}_4\text{I}_4$ requires $\text{Cl} = 19.90$ per cent.

The compound slowly evolves chlorine on exposure to the air, until one atomic proportion has been lost (no evolution of hydrochloric acid was detected) as shown by the following results : a specimen which had remained in an open * bottle for five weeks gave $\text{Cl} = 15.52$.

The same specimen after three months gave $\text{Cl} = 15.44$.

$\text{C}_4\text{HNCI}_3\text{I}_4$ requires $\text{Cl} = 15.47$ per cent.

This substance melts at $158-159^\circ$, without evolution of chlorine, to an orange-red liquid, and decomposes at 185° with evolution of iodine vapour.

When treated with sodium hydroxide, the compound changes from a bright to a pale yellow colour, excess of alkali produces a solution which becomes deep purple-red after a few minutes ; these changes have not yet been investigated beyond the recognition of the fact that the chlorine is removed by the alkali as chloride and hypochlorite, whilst the iodine remains united to the pyrrole nucleus.

Action of Chlorine on Trimethylsulphonium Iodide.

This compound is insoluble in chloroform, and very sparingly soluble in glacial acetic acid ; a solution in acetic acid containing 10 per cent. of water was used. The experiment is best carried out by allowing the solution of the sulphonium iodide to drop continually into a vessel through which a current of chlorine gas is being passed, the vessel being kept in agitation during the progress of the reaction.

As the solution meets the chlorine a momentary liberation of iodine takes place, followed almost immediately by the separation of the new compound as a bright yellow precipitate, which is easily purified from excess of chlorine by washing with chloroform in which it is quite insoluble. The superficial examination of the substance reveals a considerable resemblance to the iodochlorides ; for example, on heating, chlorine is evolved, and on addition of sodium hydroxide the compound changes at first from a bright to a pale yellow, the chlorine being partly removed as chloride and hypochlorite. The further addition of alkali, however, effects a complete solution with removal of the iodine as iodide and iodate, in which respect the substance differs entirely from the iodochlorides prepared from benzene derivatives.

The analyses of the compound show that its composition is to be represented by the formula $(\text{CH}_3)_3\text{SCI,ICl}_2$.

* It is well known that the iodochlorides keep much better when freely exposed to the air ; for instance, the compound $\text{C}_6\text{H}_5\cdot\text{ICl}_2$ may be kept for months practically unchanged in an open dish, whilst, if placed in a closed bottle, it will undergo almost complete decomposition in about a fortnight or three weeks ; I have noticed this also in the case of several other iodochlorides.

The following method was found to be the most convenient and accurate for the rapid estimation of the iodine in this and all the succeeding compounds.

The substance is dissolved in a slight excess of sodium hydroxide solution by gently warming, the cold solution is rendered faintly acid by addition of dilute sulphuric acid, and sulphurous acid is added drop by drop until the iodine at first liberated is just redissolved. The liquid, contained in a Würtz distillation flask, is treated with an excess of neutral ferric sulphate solution, the liberated iodine is then distilled into a solution of potassium iodide and estimated in the usual way.

0.5128 gave 0.1895 iodine. $I = 36.95$.

$C_3H_9Cl_4IS$ requires $I = 36.70$ per cent.

When heated, this compound gradually evolves chlorine, the evolution being very rapid at 80° , and continuing up to 155° , when the substance melts; at 168° decomposition takes place with sudden evolution of iodine vapours, accompanied by a strong odour of methyl sulphide.

When carefully treated with two molecular proportions of sodium hydroxide, two atoms of chlorine are removed and the stable compound, $(CH_3)_3SCl, ICl$ (m. p. 103°), is formed.

0.25 gave 0.1158 of iodine. $I = 46.32$.

$C_3H_9Cl_2IS$ requires $I = 46.18$ per cent.

The constitution of this substance is proved by the fact that it is most readily prepared by simply adding a solution of Schützenberger's compound to one of trimethylsulphonium chloride; it crystallises from the hot solution on cooling in brilliant, slender, golden-yellow plates having a satiny lustre; its identity with the above was proved by analysis and melting point.

The corresponding *ethyl* compound, $(C_2H_5)_3SCl, ICl$, is a viscid, orange liquid.

Action of Chlorine on Pyridine Ethyl Iodide, C_5H_5N, C_2H_5I .

This compound, originally prepared by Anderson (*Annalen*, 1855, 94, 364), forms large prisms melting at 236° (not hitherto recorded).

When chlorine is allowed to act on a solution of this substance in a mixture* of glacial acetic acid and carbon tetrachloride, employing the same method of procedure as in the case of the sulphonium compound, there is momentary liberation of iodine, immediately followed by the separation of the *addition compound*. This is a bright canary-yellow, microcrystalline powder.

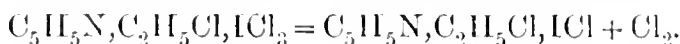
* This solution is more stable than when acetic acid alone is used.

0.2047 gave 0.0685 iodine. $I = 33.46$.

$C_7H_{10}NCl_4I$ requires $I = 33.68$ per cent.

On heating, chlorine is given off at 50° , and continues regularly up to 130 — 150° , when the evolution of gas ceases, until at 195° decomposition sets in again with further evolution of chlorine and iodine vapours.

The first stage of the decomposition corresponds to a loss of one molecular proportion of chlorine in accordance with the equation



The chlorine evolved in two experiments was 17.97 and 18.16, the equation requiring a loss of $Cl = 18.83$ per cent.

The residue crystallised from alcohol in long, orange-yellow, acicular prisms melting at 35° .

0.6295 gave 0.26035 iodine. $I = 41.35$.

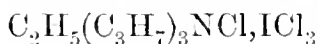
0.9058 „ 34.7 c.c. nitrogen at 14.6° and 773.2 mm. $N = 4.57$.

$C_7H_{10}NCl_2I$ requires $I = 41.50$; $N = 4.57$ per cent.

This compound was also directly prepared by the action of a solution of Schützenberger's compound on pyridine ethyl chloride in aqueous solution.

Action of Chlorine on Ethyltripropylammonium Iodide.

This substance was prepared from ethyl iodide and tripropylamino; it crystallises from alcohol in small prisms, melting at 238° with decomposition. By the action of chlorine the *compound*



is obtained as a pale yellow powder.

0.2145 gave 0.0626 iodine. $I = 29.13$.

$C_{11}H_{23}NCl_4I$ requires $I = 28.80$ per cent.

When heated, evolution of chlorine commences at 81° and continues slowly up to 105° ; between this temperature and 130° gradual fusion takes place, whilst the gas is freely evolved; no further evolution of gas takes place until the temperature reaches 185° , when iodine vapours appear. The first stage of the decomposition is here again accompanied by the loss of one molecular proportion of chlorine, with production of the *compound* $C_2H_5(C_3H_7)_3NCl, ICl$.

5.0 lost 0.79 chlorine. $Cl = 15.8$.

$C_{11}H_{23}NCl_4I$ requires a loss of $Cl = 16.09$ per cent.

The *dichloro*-compound crystallises from alcohol in pale yellow conglomerates of acicular prisms melting at 94° .

0.16 gave 0.0548 iodine. $I = 34.25$.

0.207 „ 0.1636 AgCl. $Cl = 19.54$.

$C_{11}H_{26}NCl_2I$ requires $I = 34.32$; $Cl = 19.21$ per cent.

This compound was also prepared by the direct action of a solution of Schützenberger's compound on ethyltripropylammonium chloride, and also by the action of sodium hydroxide (two molecular proportions) on the original chlorine compound.

Action of Chlorine on Phenyl dimethylethylammonium Iodide.

This experiment was made with the object of ascertaining if the presence of the phenyl group in direct union with nitrogen would produce any appreciable change in the general nature of the reaction.

The addition compound, $C_6H_5(CH_3)_2C_2H_5NCl, ICl_3$, separates from a mixture of chloroform and glacial acetic acid as a bright orange powder.

0.5 gave 0.1537 iodine. $I = 30.73$.

$C_{10}H_{16}NCl_4I$ requires $I = 30.31$ per cent.

On heating, the substance gradually fuses between 90° and 110° with evolution of chlorine.

It may be concluded, as a result of the foregoing experiments, that when chlorine acts on the sulphonium and substituted ammonium iodides, compounds of the general type RCI, ICl_3 are produced, and, further, that the tendency towards the formation of these substances is so strong that iodine trichloride is formed almost as rapidly as the iodine is liberated.

It is worthy of note that these compounds may also be prepared even in aqueous solution; this is interesting considering that iodine trichloride is so readily decomposed by water. This fact might be used as an argument in favour of the view that they are derivatives of quinquivalent iodine rather than molecular compounds.

The compounds of the general type RCI, ICl are only stable in aqueous solution when hydrochloric acid is present.

The following compounds, in addition to those already described, were prepared in order to prove that their existence is general:

$(CH_3)_4NCl, ICl$, yellow crystals, melting at 217° .

0.25 gave 0.1164 iodine. $I = 46.56$.

$C_4H_{12}NCl_2I$ requires $I = 46.69$ per cent.

$(C_2H_5)_4NCl, ICl$, lustrous, golden-yellow plates melting at 98° .

0.25 gave 0.0965 iodine. $I = 38.60$.

$C_6H_{20}NCl_2I$ requires $I = 38.71$ per cent.

$(C_3H_7)_2H_2NCl, ICl$ separates as an orange-red liquid, which slowly forms deliquescent crystals melting at 45° .

0.25 gave 0.1066 iodine. $I = 42.64$.

$C_6H_{16}NCl_2I$ requires $I = 42.33$ per cent.

$(C_3H_7)_3HNCl, ICl$, deliquescent, pale orange crystals melting at 42° .

0.4 gave 0.1479 iodine. $I = 36.98$.

$C_9H_{22}NCl_2I$ requires $I = 37.13$ per cent.

$(C_7H_7)H_3NCl, ICl$, brilliant, golden-yellow, slender prisms melting at 110°

0.25 gave 0.10414 iodine. $I = 41.65$.

$C_7H_{10}NCl_2I$ requires $I = 41.57$ per cent.

Thus primary, secondary, and tertiary amines form compounds just as readily as the quaternary bases.

These substances are precipitated when a solution of Schützenberger's compound is added to the aqueous solution of the hydrochloride of the base.

From an aqueous solution of hexamethylenetetramine in presence of hydrochloric acid, the *compound* $(CH_2)_6N_4(ICI)_2$ is precipitated as a pale sulphur-yellow, amorphous powder melting at $161-162^\circ$ with evolution of iodine.

0.25 gave 0.1347 iodine. $I = 53.8$.

$C_6H_{12}N_4Cl_2I_2$ requires $I = 54.15$ per cent.

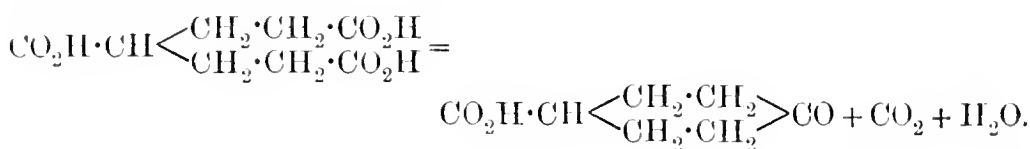
In conclusion I desire to express my thanks to my friend Mr. William Caldwell, M.A., for his valuable assistance in connection with both the experimental and analytical work recorded in this paper.

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CLXV.—*Experiments on the Synthesis of the Terpenes.*
Part LX. The Preparation of cyclopentanone-4-carboxylic Acid and of cyclohexanone-4-carboxylic Acid (δ-Ketohexahydrobenzoic Acid).

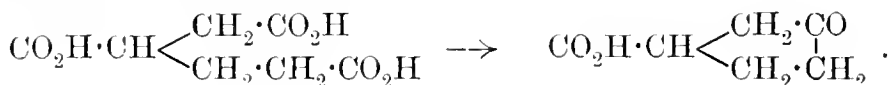
By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun.

IN a previous communication (Trans., 1904, 85, 418) it was shown that δ-ketohexahydrobenzoic acid (*cyclohexanone-4-carboxylic acid*) is formed when pentane-αγδ-tricarboxylic acid is digested with acetic anhydride and then distilled:



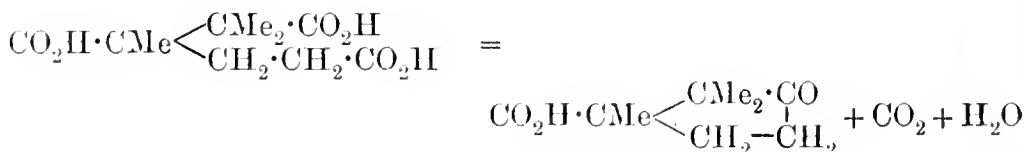
This method of preparation is very laborious, because the decomposition cannot conveniently be carried out with more than 10 grams of the tricarboxylic acid at a time and because the yield of keto-acid obtained is, at the most, 30 per cent. of the theoretical.

Several months, indeed, had to be spent in the preparation of the quantity of δ-ketohexahydrobenzoic acid (about 300 grams) which was required in order to carry out the experiments on the synthesis of terpineol, dipentene, &c. (Trans., 1904, 85, 656). While these experiments were in progress, many attempts were made to obtain the corresponding *cyclopentanone-4-carboxylic acid* from butane-αβδ-tricarboxylic acid by a similar series of reactions:



These were all unsuccessful, since the tricarboxylic acid did not yield more than traces of a keto-acid when it was heated alone or when it was digested with acetic anhydride and then distilled.

The reason for this difference in behaviour is difficult to understand, especially in view of the fact that homocamphoronic acid (which is a trimethyl-substitution product of butane-αβδ-tricarboxylic acid) is converted into camphoronic acid when it is slowly distilled:



(Lapworth and Chapman, Trans., 1900, 77, 464).

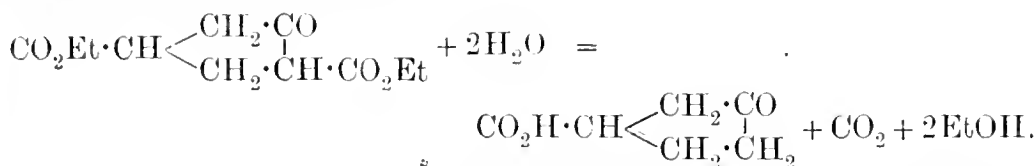
As, however, *cyclopentanone-4-carboxylic acid* was essential as a starting point for further synthetical experiments in the camphor and terpene series, we investigated many other methods which appeared likely to lead to a method of preparation and were ultimately successful. Dieckmann (*Ber.*, 1894, 27, 102, 965) had shown that ethyl adipate readily undergoes intramolecular condensation when it is heated with sodium with formation of ethyl *cyclopentanone-2-carboxylate*:



Since ethyl butane- $\alpha\beta\delta$ -tricarboxylate is a substitution derivative of ethyl adipate, it seemed possible that a similar condensation would take place if it were treated with sodium under similar conditions:



This was found to be the case, and the resulting *ethyl cyclopentanone-2:4-dicarboxylate*, which we have prepared by this method in large quantities, is readily decomposed by boiling with dilute sulphuric acid, with elimination of carbon dioxide and alcohol and formation of *cyclopentanone-4-carboxylic acid*:

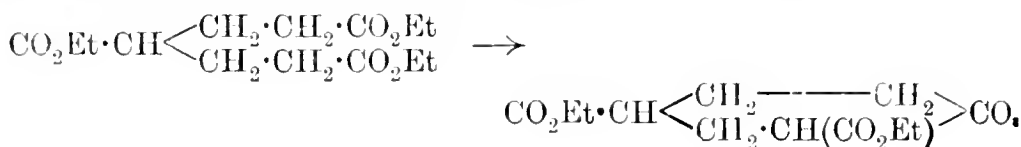


This interesting acid melts at 65° and shows all the properties of a keto-acid. It yields an oxime and a semicarbazone and is readily reduced by sodium amalgam, but the detailed description of its other properties must be reserved for a future communication.

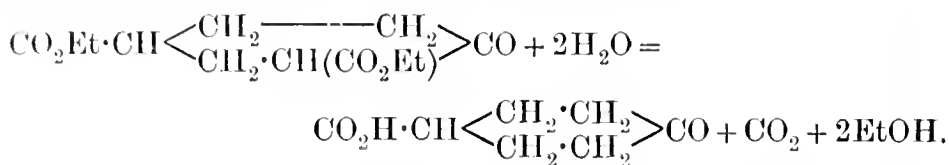
It is hoped that this acid may serve as a convenient starting point for a new series of synthetical experiments in the camphor and terpene series.

The method, which has so far been the only one available for the preparation of δ -keto-hexahydrobenzoic acid, is, as has already been mentioned, exceedingly laborious, and the above experiments suggested that this important acid might possibly be more readily prepared by employing a process similar to that which had proved so successful in the case of *cyclopentanone-4-carboxylic acid*.

We therefore investigated the action of sodium on ethyl pentane- $\alpha\gamma\epsilon$ -tricarboxylate and found that the decomposition proceeded normally and with the formation of *ethyl cyclohexanone-2:4-dicarboxylate*:



When this ester is digested with dilute sulphuric acid, it is readily decomposed with formation of δ -ketohexahydrobenzoic acid,

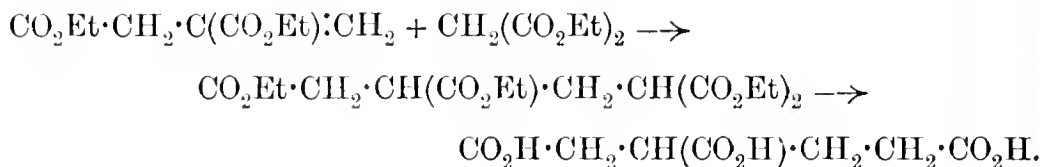


This new method of preparation, although still laborious, is more rapidly carried out, and gives a much better yield than that described at the commencement of this paper.

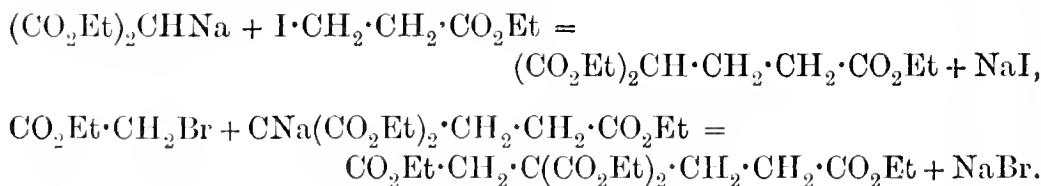
EXPERIMENTAL.

Butane- $\alpha\beta\delta$ -tricarboxylic Acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

This acid was first prepared in small quantities by Auwers, Köbner, and Meyenburg (*Ber.*, 1891, **24**, 2895) by condensing ethyl itaconate with the sodium derivative of ethyl malonate, and the subsequent hydrolysis of the ethyl butane- $\alpha\beta\delta\delta$ -tetracarboxylate thus produced :



It was subsequently obtained by Guthzeit and Engelmann (*J. pr. Chem.*, 1902, **66**, 104; compare Emery, *Ber.*, 1891, **24**, 282), who prepared it from ethyl malonate by the following series of reactions :



The ethyl butane- $\alpha\beta\delta$ -tetracarboxylate thus produced yielded butane- $\alpha\beta\delta$ -tricarboxylic acid when it was digested with dilute hydrochloric acid. In order that the experiments described in this paper could be carried out, it was necessary to employ large quantities of this butanetricarboxylic acid, and we therefore instituted a series of comparative experiments with the object of discovering the most satisfactory method of preparation. We found that the process described by Guthzeit and Engelmann (*loc. cit.*) gave the best results, with, however, the important modification that the sodium derivative of ethyl malonate is first treated with ethyl bromoacetate and then with ethyl β -iodopropionate. When ethyl β -iodopropionate reacts with the sodium derivative of ethyl malonate, there is much loss of valuable iodo-ester

owing to elimination of hydrogen iodide and formation of ethyl acrylate. If, however, ethyl ethanetricarboxylate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, is first prepared and the sodium derivative of this ester treated with ethyl β -iodopropionate, elimination of hydrogen iodide from the latter takes place only to a slight extent. The details of the preparation are as follows.

Sodium (23 grams) is dissolved in absolute alcohol (350 c.c.), and, after cooling, mixed with ethyl malonate (160 grams) and ethyl bromoacetate (160 grams),* the vigorous reaction being controlled by cooling in running water. After isolating in the usual way, the ethyl ethanetricarboxylate, $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is separated from the ethyl propanetetracarboxylate, $(\text{CO}_2\text{Et})_2\text{C}:(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, which is always produced, by repeated fractionation under reduced pressure. The average yield of ethyl ethanetricarboxylate distilling at $160\text{--}176^\circ$ (15 mm.) was about 140–150 grams. This ester (246 grams) is now mixed with a well-cooled solution of sodium (23 grams) in alcohol (350 c.c.), and then ethyl β -iodopropionate (228 grams) gradually added, care being taken that the temperature does not rise above 35° , otherwise some of the iodo-ester will be decomposed with formation of acrylic ester. After remaining for twenty-four hours, the product is heated on the water-bath for half an hour, mixed with water, and extracted with ether. The ethereal solution is well washed with water, dried over calcium chloride, evaporated, and the ethyl butane- $\alpha\beta\delta$ -tetracarboxylate purified by fractionation under reduced pressure, when almost the whole quantity distils at $200\text{--}203^\circ$ (12 mm.), the yield being about 85 per cent. of that theoretically possible.

0.1562 gave 0.3171 CO_2 and 0.1056 H_2O . $\text{C} = 55.3$; $\text{H} = 7.5$.

$\text{C}_{16}\text{H}_{26}\text{O}_8$ requires $\text{C} = 55.5$; $\text{H} = 7.5$ per cent.

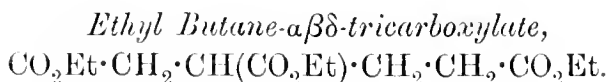
Hydrolysis.—When ethyl butane- $\alpha\beta\delta$ -tetracarboxylate is digested with hydrochloric acid it is directly converted, by hydrolysis and elimination of carbon dioxide, into butane- $\alpha\beta\delta$ -tricarboxylic acid. The ester (150 grams) is mixed with concentrated hydrochloric acid (300 c.c.), and heated to boiling in a large flask fitted with a ground-in tube in such a way that the alcohol formed by hydrolysis escapes through

* The theoretical amount is 167 grams, but the smaller quantity is employed in order to ensure that no ethyl bromoacetate is left after the reaction is complete. If the theoretical quantity is used, some ethyl bromoacetate is liable to remain unchanged and when the product of the reaction is worked up, the presence of even traces of this bromo-ester exerts, as is well known, a most painful action on the eyes and skin. Unfortunately, if ethyl chloroacetate is employed, the yield of ethyl ethanetricarboxylate is not much more than half that obtained when the bromo-ester is used owing to the formation of larger quantities of ethyl propanetetracarboxylate, $(\text{CO}_2\text{Et})_2\text{C}:(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ (compare Bischhoff and Kuhlberg, *Ber.*, 1890, **23**, 634).

the end of the tube. After about an hour, most of the oil will have passed into solution, and at this stage the evolution of carbon dioxide is sometimes so vigorous that care has to be taken to avoid loss by frothing. The heating is continued for six hours, water (150 c.c.) is then added, and the liquid boiled for a further six hours, and then evaporated as far as possible on the water-bath. The syrupy residue gradually crystallises and ultimately becomes almost solid and, if the mass is then left in contact with porous porcelain for a couple of days, the colourless crystalline cake consists of almost pure butane- $\alpha\beta\delta$ -tricarboxylic acid. A small quantity of the acid was further purified by crystallisation from acetone, from which it separated in prisms melting at 116—118°.

0.1452 gave 0.2355 CO₂ and 0.0704 H₂O. C = 44.3 ; H = 5.4.

C₇H₁₀O₆ requires C = 44.2 ; H = 5.3 per cent.

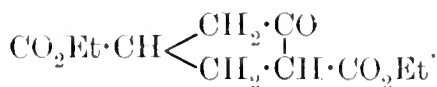


This ester is best prepared from the crude syrupy tribasic acid (as obtained by evaporating the product of the hydrolysis of ethyl butane- $\alpha\beta\delta$ -tetracarboxylate on the water-bath), but some difficulty was experienced in obtaining a good yield owing to the fact that, when the alcoholic solution of the acid is treated with hydrogen chloride in the usual manner, a good deal of the acid is only partially esterified. The best results were obtained by digesting the acid (100 grams) with alcohol (500 c.c.) and sulphuric acid (50 c.c.) for two days on the water-bath. The product is mixed with much ether, the ethereal solution washed with water and extracted several times with sodium carbonate, the sodium carbonate solution, which contains much partially esterified acid, is evaporated to dryness and treated directly with alcohol and sulphuric acid, this operation being repeated until the whole of the tribasic acid has been converted into the neutral ester. The ester is then purified by fractionation under reduced pressure, when almost the whole quantity passes over at 183—185° (20 mm.) or at 205—206° (60 mm.).

0.1511 gave 0.3142 CO₂ and 0.1091 H₂O. C = 56.6 ; H = 8.0.

C₁₃H₂₂O₆ requires C = 56.9 ; H = 8.0 per cent.

Action of Sodium on Ethyl Butane- $\alpha\beta\delta$ -tricarboxylate. Formation of Ethyl cyclopentanone-2:4-dicarboxylate,



In carrying out this condensation, sodium (23 grams) is melted under boiling toluene and shaken vigorously in order to bring it into as fine a state of division as possible. The toluene is then poured off, the sodium washed into a 2-litre flask with dry benzene, ethyl butane- $\alpha\beta\delta$ -tricarboxylate (137 grams) diluted with twice its volume of benzene is added, and after attaching a long reflux condenser the whole is gradually heated on the water-bath. In a short time the reaction commences and may become so vigorous as to necessitate cooling with water; ultimately the decomposition is completed by heating on the water-bath until the sodium has completely dissolved. The yellow product is decomposed by dilute hydrochloric acid and ice, the oily layer separated, washed well with sodium carbonate, dried over calcium chloride and fractionated under reduced pressure. After the benzene has passed over, the residue distils almost completely at 160—170° (18 mm.), and, after refractionating, a portion boiling at 166° (18 mm.) gave the following results on analysis:

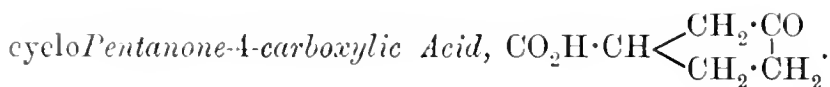
0.1843 gave 0.3920 CO_2 and 0.1160 H_2O . C=58.1; H=7.0.

0.1656 „ 0.3537 CO_2 „ 0.1053 H_2O . C=58.2; H=7.1.

$\text{C}_{11}\text{H}_{16}\text{O}_5$ requires C=57.9; H=7.0 per cent.

Ethylcyclopentanone-2:4-dicarboxylate is a colourless oil with a pale blue fluorescence and an odour somewhat resembling that of ethyl acetoacetate. Its alcoholic solution is coloured an intense crimson by the addition of ferric chloride. The yield of the pure keto-ester from the quantities stated above is often only about 50 grams, or not more than 45 per cent. of the theoretical amount. This is due to the fact that a large quantity of dark coloured oil is extracted by the treatment with sodium carbonate. If this alkaline extract is acidified with dilute sulphuric acid and heated to boiling under the conditions described in the next section, considerable quantities of crude cyclopentanone-4-carboxylic acid may be extracted with ether.

This crude acid is best purified by esterification and fractionation of the ester under reduced pressure.



This acid is formed from ethyl *cyclopentanone-2:4*-dicarboxylate by hydrolysis and elimination of carbon dioxide, a change which is readily brought about by boiling with dilute mineral acids, but the acid employed must be very dilute, because concentrated acids such as hydrochloric acid give rise to the formation of uncrystallisable resins of high molecular weight. The ester is digested with ten times its volume of 8 per cent. sulphuric acid in a flask fitted with a ground-in condenser for about three hours and until solution is complete. The clear liquid is neutralised with sodium carbonate, evaporated on the water-bath until free from alcohol, acidified, saturated with ammonium sulphate, and extracted with ether at least ten times, preferably on the shaking machine. After drying over calcium chloride and evaporating, a viscid gum is obtained which, with the exception of a small quantity of substance of high boiling point, distils almost constantly at 197° (30 mm.). The distillate sometimes remains liquid for several days, but if a crystal of the keto-acid is introduced, the whole is rapidly converted into a solid mass. For analysis, the substance was crystallised from benzene.

0.1370 gave 0.2823 CO_2 and 0.0767 H_2O . C = 56.2; H = 6.2.

0.1501 „ 0.3106 CO_2 „ 0.0845 H_2O . C = 56.4; H = 6.3.

$\text{C}_6\text{H}_5\text{O}_3$ requires C = 56.3; H = 6.2 per cent.

cycloPentanone-4-carboxylic acid crystallises from benzene, in which it is very readily soluble, in hard crusts melting at $64\text{--}65^\circ$. It dissolves readily in water and in most organic solvents, but is sparingly soluble in light petroleum. The basicity of the acid was determined by titration with decinormal caustic potash, when 0.3242 neutralised 0.1417 KOH, whereas this amount of a monobasic acid, $\text{C}_6\text{H}_8\text{O}_3$, should neutralise 0.1419 KOH.

The Oxime.—In order to prepare this derivative, the pure acid (2 grams), dissolved in the minimum quantity of water, was mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (2 grams) and caustic potash (4 grams) and allowed to stand for three days. The alkaline solution was acidified and extracted at least twenty times with ether, the extract was dried over calcium chloride and evaporated, when a yellow oil was obtained which soon solidified. After remaining in contact with porous porcelain until quite dry, the oxime was recrystallised from ether, in which it is sparingly soluble.

0.1230 gave 10.2 c.c. of nitrogen at 18° and 766 mm. N = 9.5.

$\text{C}_6\text{H}_9\text{O}_3\text{N}$ requires N = 9.8 per cent.

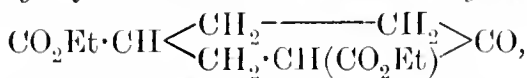
1-*Oximinocyclopentanone* 1-carboxylic acid is a colourless, crystalline solid which melts at 111° and is very readily soluble in water or alcohol, but sparingly so in benzene or light petroleum.

The *semicarbazone* separates gradually in nodular masses when a concentrated aqueous solution of the acid is mixed with semicarbazido hydrochloride and sodium acetate. It dissolves readily in boiling water, and crystallises on cooling in hard crusts which decompose at about 190° .

0.2573 gave 51.1 c.c. of nitrogen at 19° and 767 mm. $N = 23.0$.

$C_7H_{11}O_3N$ requires $N = 22.7$ per cent.

Ethyl cycloHexanone-2:4-dicarboxylate,



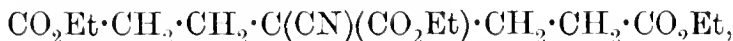
and *cycloHexanone-4-carboxylic Acid* (δ -*Ketoheptahydrobenzoic Acid*),



The ethyl pentane- $\alpha\gamma\epsilon$ -tricarboxylate,



which was required for the following experiments had not previously been described, but it may be conveniently prepared as follows. Ethyl- γ -cyanopentane- $\alpha\gamma\epsilon$ -tricarboxylate,



prepared by the action of ethyl β -iodopropionate on the sodium derivative of ethyl cyanoacetate (Trans., 1904, 85, 422), is digested in quantities of 100 grams with concentrated hydrochloric acid (200 c.c.) for several hours and until the evolution of carbon dioxide has ceased (compare p. 1643).

Water (100 c.c.) is then added, and, after boiling for six hours, the whole is evaporated to dryness and the mixture of crude pentane- $\alpha\gamma\epsilon$ -tricarboxylic acid and ammonium chloride digested for two days with alcohol (300 c.c.) and sulphuric acid (30 c.c.), the product being then treated exactly as described in the case of the preparation of ethyl butane- $\alpha\beta\delta$ -tricarboxylate (p. 1644). Ethyl pentane- $\alpha\gamma\epsilon$ -tricarboxylate is a colourless oil, which distils at 195° (20 mm.) and at 210° (50 mm.).

0.2568 gave 0.5431 CO_2 and 0.1982 H_2O . $C = 57.8$; $H = 8.7$.

$C_{14}H_{24}O_6$ requires $C = 58.3$; $H = 8.3$ per cent.

Ethyl cycloHexanone-2:4-dicarboxylate.—The preparation of this keto-ester by the action of sodium (23 grams) on ethyl pentane- $\alpha\gamma\epsilon$ -tricarboxylate (144 grams) was carried out in benzene solution under

conditions substantially the same as those described in the case of the preparation of ethyl cyclopentanone-2:4-dicarboxylate from ethyl butane $\alpha\beta\delta$ tricarboxylate (p. 1645).

After the product had been decomposed by hydrochloric acid, the benzene layer was separated, washed with sodium carbonate,* dried over calcium chloride, and fractionated, when almost the whole of the oil distilled at about 180° (20 mm.).

0.2117 gave 0.4693 CO_2 and 0.1444 H_2O . $\text{C} = 59.2$; $\text{H} = 7.3$.

$\text{C}_{12}\text{H}_{18}\text{O}_5$ requires $\text{C} = 59.5$; $\text{H} = 7.4$ per cent.

Ethyl cyclohexanone-2:4-dicarboxylate is a colourless oil possessing an odour closely resembling that of ethyl acetoacetate and the alcoholic solution of which is coloured an intense crimson by the addition of ferric chloride. The yield of pure keto-ester obtained under the above conditions is not more than 50 per cent. of that theoretically possible.

cycloHexanone-4-carboxylic Acid (δ -Ketohexahydrobenzoic Acid).—This acid is readily obtained when ethyl cyclohexanone-2:4-dicarboxylate is digested with dilute sulphuric acid (10 per cent.) for two or three hours and until the evolution of carbon dioxide has ceased.

The clear liquid is then neutralised with sodium carbonate and evaporated with the frequent addition of small quantities of water until quite free from alcohol; it is then acidified and saturated with ammonium sulphate, when the keto-acid soon separates as a voluminous precipitate. This precipitate is collected at the pump, dried over sulphuric acid in an evacuated desiccator, and the keto-acid separated from inorganic matter by extracting several times with boiling light petroleum. The light petroleum is then removed by distillation, the residue, which soon crystallises, left in contact with porous porcelain until quite dry, and finally crystallised from a mixture of benzene and light petroleum.

0.1369 gave 0.2952 CO_2 and 0.0872 H_2O . $\text{C} = 58.8$; $\text{H} = 7.1$.

$\text{C}_7\text{H}_{10}\text{O}_3$ requires $\text{C} = 59.1$; $\text{H} = 7.0$ per cent.

Prepared in this way, δ -ketohexahydrobenzoic acid melted at $67\text{--}68^\circ$, and proved to be identical in all respects with the acid which had previously been obtained from pentane- $\alpha\gamma\epsilon$ -tricarboxylic acid by treatment with acetic anhydride, and subsequent distillation (Trans., 1904, 85, 425).

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* When the alkaline extract was acidified with dilute sulphuric acid, boiled until the evolution of carbon dioxide had ceased, and then saturated with ammonium sulphate, the solution gradually deposited a large quantity of nearly pure δ -ketohexahydrobenzoic acid.

CLXVI.—*Some Derivatives of Catechol, Pyrogallol, Benzophenone, and of Substances allied to the Natural Colouring Matters.*

By WILLIAM HENRY PERKIN, jun., and CARL WEIZMANN.

THIS communication contains the description of a number of new substances which have been prepared at different times in connection with researches on the constitution of brazilin, hæmatoxylin, and other natural colouring matters.

It also contains the results of the investigation of a considerable number of new derivatives of benzophenone, most of which have been prepared by students in the laboratories of the University of Manchester.*

Preparation of Veratrole, $C_6H_1(OMe)_2$, and Dimethylhomocatechol
 $C_6H_3Me(OMe)_2 = 1 : 3 : 4$.

During the course of a large number of experiments on the methylation of brazilin, hæmatoxylin, and other phenolic substances by means of methyl sulphate, we have repeatedly noticed that such methylation takes place almost quantitatively if the following conditions, which we describe in the case of veratrole and dimethylhomocatechol, are observed.

(1) Catechol (100 grams) is dissolved in methyl alcohol (200 c.c.) mixed with methyl sulphate (75 grams) and, after cooling to -5° , a solution of caustic potash (150 grams) in water (350 c.c.) is added all at once. A vigorous action takes place and the methylation is complete in about three minutes.

After diluting with water, the oil is extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, evaporated, and the residue distilled, when pure veratrole is at once obtained as a crystalline mass which melts at 15° and distils at 205° . The yield is 95 per cent. of that theoretically possible.

(2) An almost quantitative yield of *dimethylhomocatechol* is readily obtained when creosol, $C_6H_3Me(OMe) \cdot OH = 1 : 3 : 4$, is treated with

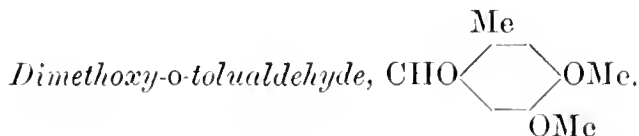
* Small investigations of this kind, carried out after the usual course of about 50 preparations, not only arouse much more interest and enthusiasm than a longer course of preparations could do, but they also serve as a valuable introduction to the methods of research and create a desire for further inquiry and original work. The share which each worker has taken is shown by attaching his name to the section for which he is responsible.

methyl sulphate and caustic potash under the above conditions. It distils at 128—130° (25 mm.) and at 216° under the ordinary pressure.

0.2750 gave 0.7258 CO₂ and 0.1900 H₂O. C = 71.5; H = 7.7.

C₉H₁₂O₂ requires C = 71.7; H = 7.9 per cent.

Large quantities of pyrogallol trimethyl ether, C₆H₃(OMe)₃, were also prepared in a similar manner, and the above conditions are especially suited to the case of phenolic substances, such as pyrogallol, which oxidise rapidly in alkaline solution.



This interesting substance, which had not previously been described, may be prepared in the following manner. Dimethylhomocatechol (40 grams) is mixed with freshly prepared and finely powdered aluminium chloride (60 grams) in a flask attached to a reflux condenser through which ice-water circulates. After cooling the flask to -5°, anhydrous hydrocyanic acid (40 grams) is added, and a slow current of dry hydrogen chloride is then passed through the cold liquid for four hours, during which operation the contents of the flask gradually solidify to a crystalline mass. After remaining for ten hours, hydrogen chloride is again passed for two hours, the flask being removed from the freezing mixture and the temperature allowed to rise to 40°.

The product is then poured into ice and dilute hydrochloric acid, and, when the aluminium compound has been completely decomposed, the whole is extracted with ether and the ethereal solution shaken four or five times with fresh quantities of sodium hydrogen sulphite. The extract is then decomposed by sodium carbonate, when the new aldehyde separates as an oil which soon crystallises.

For analysis, the substance was crystallised from methyl alcohol.

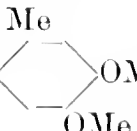
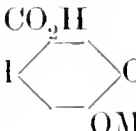
0.1385 gave 0.3381 CO₂ and 0.0836 H₂O. C = 66.6; H = 6.7.

C₁₀H₁₂O₃ requires C = 66.7; H = 6.7 per cent.

4:5-Dimethoxy-*o*-tolualdehyde separates from methyl alcohol in colourless needles, melts at 76°, and has an odour similar to that of vanillin. The yield obtained in the above process was about 35 per cent. of that theoretically possible. When the aldehyde, dissolved in methyl alcohol, is mixed with a concentrated aqueous solution of semicarbazide hydrochloride and sodium acetate, the *semicarbazone* separates as a crystalline powder which crystallises from methyl alcohol in leaflets and melts at 216—218°.

The *hydrazone* separates in yellow needles when the alcoholic solution of the aldehyde is mixed with phenylhydrazine and allowed to stand for twenty-four hours. It melts at 118° .

Oxidation of Dimethoxy-o-tolualdehyde. Formation of Dimethoxy-o-

toluic Acid, CO_2H , and *m-Hemipinic Acid*, CO_2H .

In studying this oxidation, the aldehyde (9 grams) was ground with water to a fine paste and oxidised at the ordinary temperature with a 2 per cent. solution of potassium permanganate (22 grams). After heating to boiling and filtering, the filtrate and washings of the manganese precipitate were concentrated and acidified, when a solid acid separated which, after crystallising from much water, yielded the following results on analysis :

0.1901 gave 0.4266 CO_2 and 0.1037 H_2O . $\text{C} = 61.2$; $\text{H} = 6.1$.

$\text{C}_{10}\text{H}_{12}\text{O}_4$ requires $\text{C} = 61.2$; $\text{H} = 6.1$ per cent.

4:5-Dimethoxy-o-toluic acid melts at 145° with decomposition and is almost insoluble in cold water ; it dissolves, however, appreciably in boiling water and separates, on cooling, as a voluminous mass of needles.

The mother liquors from a number of preparations of dimethoxy-o-toluic acid were concentrated, repeatedly extracted with ether, and the extract evaporated, when a solid remained which was found to be a mixture of dimethoxy-o-toluic acid and *m*-hemipinic acid. These acids were separated by repeated recrystallisation from water, and pure *m*-hemipinic acid was thus obtained in hard, colourless prisms which contained water of crystallisation.

The anhydrous acid gave the following results on analysis :

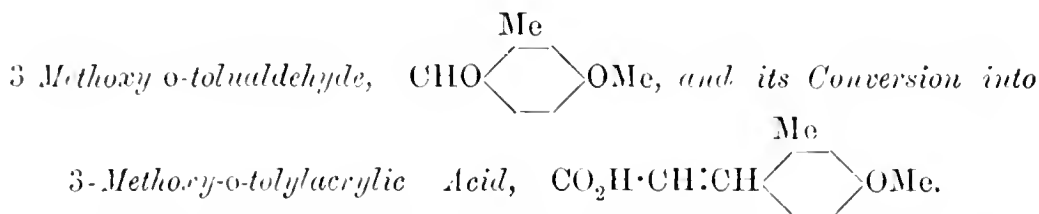
0.2130 gave 0.4139 CO_2 and 0.0884 H_2O . $\text{C} = 53.0$; $\text{H} = 4.6$.

$\text{C}_{10}\text{H}_{10}\text{O}_6$ requires $\text{C} = 53.1$; $\text{H} = 4.5$ per cent.

That this acid was *m*-hemipinic acid was conclusively proved by converting it into the characteristic ethylimide (Goldschmiedt, *Monatsh.*, 1888, 9, 339), which was sparingly soluble in alcohol and melted at 230° .

The yield of this acid was small, and experiments which were made with the object of increasing the yield (by using larger quantities of permanganate and of other oxidising agents) were only partially successful. This is due to the slight tendency which the methyl group in dimethoxy-o-toluic acid exhibits to become oxidised to the carboxyl group, and if large quantities of oxidising agent are

employed at the temperature of the water-bath, some of the acid escapes oxidation and most of the remainder is completely decomposed, with formation of much oxalic acid.



The methoxy-*o*-tolualdehyde, employed in these experiments, was prepared as follows: *m*-cresol methylether (25 grams), was mixed with anhydrous hydrocyanic acid (30 grams), cooled to -5° , and powdered aluminium chloride (20 grams) gradually added. Dry hydrogen chloride was then passed for five hours at 0° , and then at the ordinary temperature for two hours. The crystalline mass which separated was decomposed with ice and dilute hydrochloric acid, the solution extracted with ether, the ethereal extract shaken with sodium hydrogen sulphite, and the crystalline bisulphite compound which separated decomposed by sodium carbonate. The aldehyde was then recrystallised from methyl alcohol.

*3-Methoxy-*o*-tolylacrylic Acid*.—The ester of this acid is readily obtained and in a good yield by employing a method similar to that described by Claisen (*Ber.*, 1890, **23**, 976) for the preparation of ethyl cinnamate.

Methoxy-*o*-tolualdehyde (1 mol.), is dissolved in pure ethyl acetate (5 mols.), and molecular sodium* ($1\frac{1}{2}$ mols.) added, when a brisk reaction soon sets in which is moderated by cooling the flask in ice-water. After remaining for twenty-four hours, the product is treated with dilute acetic acid, the oil extracted with ether, and the ethereal solution dried and evaporated. The brown oil is left over sulphuric acid in an evacuated desiccator until semi-solid, the mass is then drained on porous porcelain, and the crude ethyl methoxy-*o*-tolylacrylate hydrolysed by boiling with excess of methyl-alcoholic potash.

After adding water and evaporating until free from methyl alcohol, the alcoholic solution is acidified, when the new acid separates as a sparingly soluble, crystalline precipitate, and is purified by crystallisation from acetic acid.

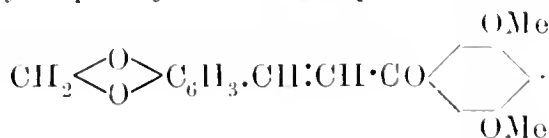
0.1648 gave 0.4132 CO_2 and 0.0889 H_2O . C = 68.5; H = 6.0.

$\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C = 68.8; H = 6.2 per cent.

* Prepared by melting sodium under boiling toluene and vigorously shaking (compare *Trans.*, 1906, **89**, 783).

3-Methoxy-o-tolylacrylic acid melts at about 185°, and is almost insoluble in cold water. It dissolves, however, appreciably in boiling water and separates on cooling in voluminous colourless needles; it is also readily soluble in acetic acid.

*Condensation of Resacetophenone Dimethyl Ether with Piperonal.
Formation of Piperonylideneresacetophenone Dimethyl Ether*



The resacetophenone dimethyl ether required for these experiments was prepared by methylating resacetophenone in methyl-alcoholic solution with methyl sulphate and caustic potash according to the directions given on p. 1649.

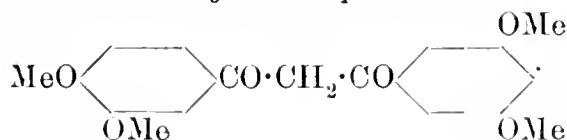
Molecular proportions of piperonal and resacetophenone dimethyl ether were dissolved in absolute ether and treated with molecular sodium* (1 mol.), the mixture being cooled at first in a freezing mixture, and afterwards left at the ordinary temperature for forty-eight hours. The reaction was then completed by heating at 30–40° for two days; the yellow crystals were then collected and purified by recrystallisation from acetic acid.

0.2090 gave 0.5288 CO₂ and 0.1040 H₂O. C = 69.1; H = 5.4.

C₁₃H₁₆O₅ requires C = 69.2; H = 5.1 per cent.

Piperonylideneresacetophenone Dimethyl ether melts at 139° and is obtained by the above process in a nearly quantitative yield.

*Condensation of Ethyl Veratrate with Resacetophenone Dimethyl Ether.
Formation of Protocatechuoylresacetophenone Tetramethyl Ether,*



When a mixture of ethyl veratrate (1 mol.), and resacetophenone dimethyl ether (1 mol.) is treated with molecular sodium (1 mol.), under the conditions described in the last section, the yellow, crystalline sodium derivative of the above condensation product is gradually deposited. This is collected, washed with ether, and then suspended in ether and cautiously decomposed by means of ice and dilute

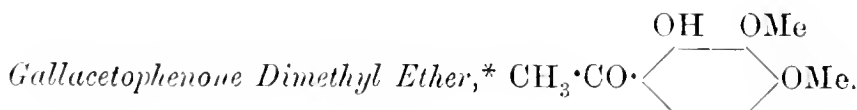
* Compare footnote, p. 1652.

hydrochloric acid. The brown ethereal solution is decolorised by animal charcoal, evaporated, and the residue crystallised from methyl alcohol.

0.1400 gave 0.3338 CO₂ and 0.0750 H₂O. C = 66.1; H = 5.9.

C₁₉H₂₀O₆ requires C = 66.3; H = 5.8 per cent.

Protocatechuoylresacetophenone Tetramethyl Ether melts at 115°, and is of special interest on account of its close relationship to brazilin, but the yield obtained by the above process is, unfortunately, so small that its detailed examination will be a matter of considerable difficulty. It dissolves readily in alcohol and gives a red coloration on the addition of ferric chloride.



This substance has been prepared in considerable quantities for use in a series of synthetical experiments which are not yet complete.

Pyrogallol trimethyl ether (30 grams) was dissolved in carbon disulphide, and, after adding acetyl chloride (16 grams), the solution was well cooled and gradually mixed with aluminium chloride (20 grams). A brisk reaction soon set in, which was moderated by cooling in ice-water, and after twenty-four hours the decomposition was complete and a deep red aluminium compound had separated.

The product was decomposed by the addition of ice and dilute hydrochloric acid, when an oil separated which soon solidified.

The crystalline mass was collected at the pump, washed well with water, and purified by recrystallisation from methyl alcohol, from which the substance separated in colourless needles melting at 77°.

0.1728 gave 0.3854 CO₂ and 0.0966 H₂O. C = 60.9; H = 6.3.

0.1384 „ 0.3096 CO₂ and 0.0768 H₂O. C = 61.1; H = 6.2.

C₁₀H₁₂O₄ requires C = 61.2; H = 6.1 per cent.

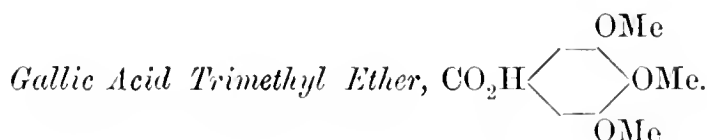
The analyses and properties of this substance clearly prove that it is gallacetophenone dimethyl ether, that is to say, one of the three methyl groups present in the pyrogallol trimethyl ether employed in its preparation has been eliminated by the hydrogen chloride formed during the above reaction. There can be little doubt that the methyl group so removed is that of the methoxy-group adjacent to the ketone group

* While the present paper was in the press, the Editor drew the attention of the authors to the fact that a gallacetophenone dimethyl ether, evidently identical with the substance here described, had already been obtained by A. G. Perkin (Trans., 1895, **67**, 997. Compare A. G. Perkin and C. R. Wilson, Proc., 1902, **18**, 215) from gallacetophenone by the action of sodium methoxide and methyl iodide. The melting point given by these authors is 77–78°.

and that the substance has the constitution given to it at the head of this section. The presence of the hydroxyl group is shown by the fact that the substance is soluble in dilute caustic potash, and that its alcoholic solution gives a deep red coloration on the addition of ferric chloride. The *hydrazone* was prepared by treating the solution of the substance in acetic acid with phenylhydrazine in the usual manner, and crystallises from methyl alcohol in pale yellow needles which melt at 171° .

0.2026 gave 0.5014 CO_2 and 0.1099 H_2O . $\text{C} = 67.4$; $\text{H} = 6.3$.

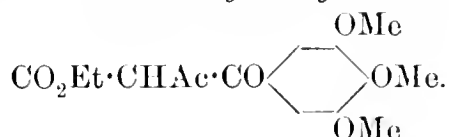
$\text{C}_{16}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{C} = 67.1$; $\text{H} = 6.3$ per cent.



Gallic acid trimethyl ether was first prepared by Graebe (*Annalen*, 1905, 340, 219), but we found that the following modification of Graebe's method was advantageous in preparing the large quantities of this acid which we required for our experiments. Gallic acid (200 grams) is dissolved in methyl alcohol (250 c.c.), methyl sulphate (300 grams) is then added, and the whole treated with a large excess of a 25 per cent. solution of caustic potash, the vigorous action being moderated by cooling in water. As soon as the decomposition is complete, the same quantities of methyl sulphate and caustic potash are again added, and after fifteen to twenty minutes the gallic acid trimethyl ether is precipitated by hydrochloric acid and purified by crystallisation from acetic acid. The yield obtained is 150—170 grams.

Gallyl chloride trimethyl ether, $(\text{MeO})_3\text{C}_6\text{H}_2\cdot\text{COCl}$, may be prepared by heating gallic acid trimethyl ether (100 grams) with phosphorus pentachloride (105 grams) on the water-bath for ten minutes. The product is distilled when the acid chloride passes over at 185° (18 mm.) and crystallises on cooling. It separates from a mixture of benzene and light petroleum in colourless needles and melts at $77-78^{\circ}$.

Ethyl 3 : 4 : 5-Trimethoxybenzoylacetacetate,



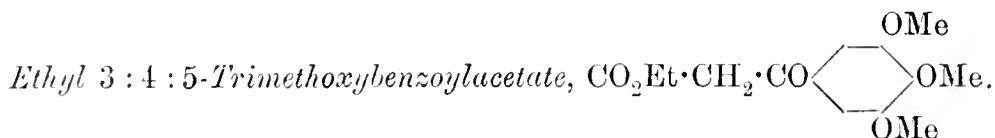
This ester was prepared by the action of gallyl chloride trimethyl ether on the sodium derivative of ethyl acetoacetate, the conditions observed being similar to those recommended by Claisen (*Annalen*,

1896, 291, 67) for the preparation of ethyl benzoylacetate. Sodium (9.2 grams) was dissolved in alcohol (150 c.c.) and 75 c.c. of this solution was added to ethyl acetoacetate (27 grams) dissolved in ether (150 c.c.). Gallyl chloride trimethyl ether (23 grams) was then dissolved in ether (150 c.c.) and 75 c.c. of this solution slowly added to the ethereal solution of the sodium derivative of ethyl acetoacetate. After remaining for half an hour, half of the remaining ethoxide and half the acid chloride solution were added, and after fifteen minutes the rest of these solutions. The product became very thick owing to the separation of salt and the sodium derivative of ethyl trimethoxybenzoylacetoacetate, and after twenty-four hours the whole was filtered at the pump, washed with ether, and decomposed by dilute hydrochloric acid, when an oil separated and soon solidified. The solid was collected, washed with water, and purified by recrystallisation from methyl alcohol.

0.1567 gave 0.3430 CO_2 and 0.0856 H_2O . $\text{C} = 59.5$; $\text{H} = 6.1$.

$\text{C}_{16}\text{H}_{20}\text{O}_7$ requires $\text{C} = 59.2$; $\text{H} = 6.2$ per cent.

Ethyl 3 : 4 : 5-trimethoxybenzoylacetoacetate melts at 85° and is readily soluble in alcohol and ether; it dissolves also in aqueous solutions of caustic potash or sodium carbonate. The alcoholic solution gives, on the addition of ferric chloride, a deep purple coloration.



In order to prepare this substance, ethyl trimethoxybenzoylacetoacetate (6 grams) is ground to a paste with water (250 c.c.), mixed with ammonium chloride (10 grams) and ammonia (50 c.c. of a 15 per cent. solution), and well shaken during ten minutes. The ester first dissolves, but an oil soon begins to separate, which rapidly solidifies, and the decomposition is hastened by gently warming on the water-bath.

The solid ester is collected, washed well, dried on porous porcelain, and purified by recrystallisation from methyl alcohol, from which it separates in leaflets.

0.1605 gave 0.3517 CO_2 and 0.0949 H_2O . $\text{C} = 59.7$; $\text{H} = 6.4$.

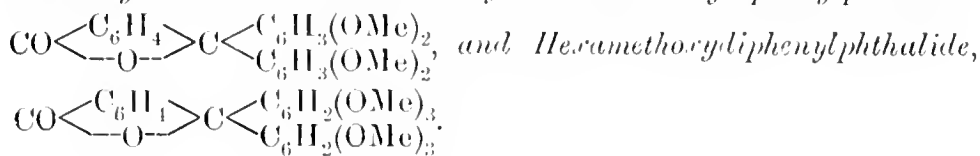
0.1566 „ 0.3425 CO_2 „ 0.0905 H_2O . $\text{C} = 59.6$; $\text{H} = 6.5$.

$\text{C}_{11}\text{H}_{15}\text{O}_6$ requires $\text{C} = 59.6$; $\text{H} = 6.4$ per cent.

Ethyl 3 : 4 : 5-trimethoxybenzoylacetoacetate melts at 95° , is readily soluble in dilute caustic potash, and its alcoholic solution gives a reddish-

violet coloration on the addition of ferric chloride. When shaken with ammoniacal copper sulphate, it yields a green copper derivative, which may be recrystallised from toluene.

Condensation of Phthalyl Chloride with Veratrole and with Pyrogallol Trimethyl Ether. Formation of Tetramethoxydiphenylphthalide,



In carrying out the first-mentioned condensation, phthalyl chloride (1 mol.) dissolved in light petroleum (b. p. 60—70°) was mixed with veratrole (2 mols.), and, after cooling in ice, finely-powdered aluminium chloride was added in small quantities at a time, the weight employed being half that of the combined weights of the phthalyl chloride and veratrole. An energetic reaction soon sets in with evolution of much hydrogen chloride, and a viscous, violet aluminium compound separates. After remaining for twelve hours in ice-water, the product is heated on the water-bath until the evolution of hydrogen chloride has practically ceased, the light petroleum is then decanted, and the aluminium compound decomposed by the addition of dilute hydrochloric acid and ice. At first, a brown oil separates, but this gradually solidifies, and, after collecting at the pump and washing with dilute hydrochloric acid and then with sodium carbonate, the residue is dried and crystallised from glacial acetic acid.

0.1442 gave 0.3702 CO₂ and 0.0692 H₂O. C = 70.5; H = 5.4.

C₂₄H₂₂O₆ requires C = 70.9; H = 5.4 per cent.

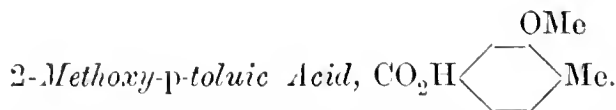
Tetramethoxydiphenylphthalide separates from acetic acid in colourless needles and melts at 155°. It is insoluble in water, sodium carbonate, or caustic potash, but dissolves in concentrated sulphuric acid, yielding a deep red solution.

The yield obtained in the above process is 65 per cent. of that theoretically possible.

Hexamethoxydiphenylphthalide was prepared by condensing phthalyl chloride with pyrogallol trimethyl ether in the presence of aluminium chloride under the same conditions as those described above in the preparation of the corresponding tetramethoxy-compound. It crystallises from acetic acid in colourless, microscopic needles and melts at 79°.

0.1764 gave 0.4308 CO₂ and 0.0952 H₂O. C = 66.6; H = 6.0.

C₂₆H₂₆O₈ requires C = 67.0; H = 5.6 per cent.



When 2-hydroxy-*p*-toluic acid (*m*-cresotic acid) is dissolved in excess of caustic potash and shaken in the cold with twice the calculated quantity of methyl sulphate, methylation not only of the hydroxy-, but also of the carboxy-group takes place, and *methyl 2-methoxy-*p*-toluate* separates as an oil. This was extracted with ether, the ethereal solution washed well, dried over calcium chloride, the ether evaporated, and the ester purified by distillation.

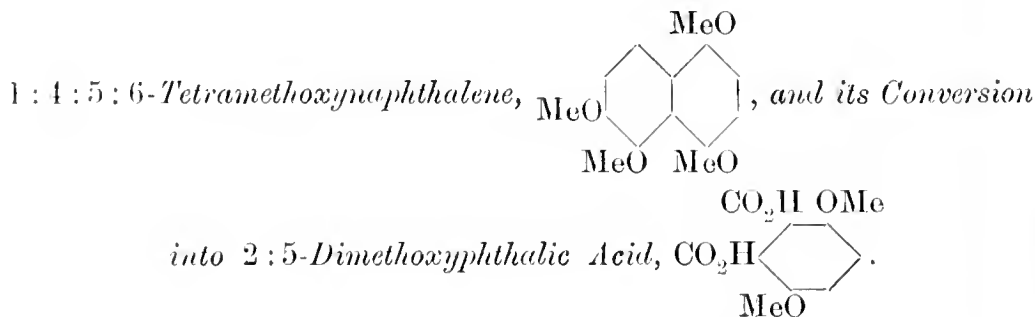
0.1844 gave 0.4503 CO_2 and 0.1062 H_2O . $\text{C} = 66.5$; $\text{H} = 6.7$.

$\text{C}_{10}\text{H}_{12}\text{O}_3$ requires $\text{C} = 66.7$; $\text{H} = 6.7$ per cent.

*Methyl 2-methoxy-*p*-toluate* is obtained in a yield of 75 per cent. in the above process; it distils at $263\text{--}265^\circ$ and has an odour resembling that of oil of gaultheria.

The alkaline solution, from which the methyl ester had been extracted, yields, on acidifying with hydrochloric acid, a precipitate of *2-methoxy-*p*-toluic acid*, which, after crystallising from acetic acid, melts at 103° , and the same acid is, of course, readily obtained from the methyl ester by hydrolysis with alcoholic potash.

We have found the above process very convenient for the methylation of salicylic, protocatechuic, β -resoreylic, and other hydroxy-acids (compare Perkin and Schiess, *Trans.*, 1904, **85**, 160), but as Graebe (*Annalen*, 1905, **340**, 204) has in the meantime given an account of similar observations, we consider it unnecessary to publish a detailed description of our experiments.



Tetramethoxynaphthalene was prepared in considerable quantities, because it was thought that it might yield hemipinic acid on oxidation, and therefore serve as a convenient starting point for the preparation of this acid. There is still no convenient method available for the preparation of this important acid, and it is therefore unfortunate that, in the present case, the oxidation should proceed in the other

possible direction with the almost exclusive formation of 2:5 di-methoxyphthalic acid.

The preparation of tetramethoxynaphthalene was accomplished as follows: 1:4:5:6-tetrahydroxynaphthalene, obtained by the reduction of naphthazarin by means of stannous chloride and hydrochloric acid (Zincke and Schmidt, *Annalen*, 1895, 286, 37), was dissolved in methyl alcohol, the solution cooled in a freezing mixture, and mixed with the calculated quantity of methyl sulphate and excess of caustic potash. When the vigorous action had subsided, half the quantities of methyl sulphate and caustic potash were added, and after remaining for twenty-four hours the product was diluted with water. The crystalline precipitate which separated was collected, washed well, and crystallised from glacial acetic acid.

0.1754 gave 0.7372 CO_2 and 0.0968 H_2O . $\text{C} = 67.9$; $\text{H} = 6.3$.

$\text{C}_{14}\text{H}_{16}\text{O}_4$ requires $\text{C} = 67.8$; $\text{H} = 6.4$ per cent.

1:4:5:6-*Tetramethoxynaphthalene* melts at about 170° and dissolves readily in acetic acid, toluene, or xylene. It separates from solvents usually in the form of grey, silky needles.

2:5-*Dimethoxyphthalic Acid*.—In investigating the oxidation of tetramethoxynaphthalene, the pure substance was ground to a very fine paste with water, a little sodium carbonate was added, and the whole was then shaken on the machine with the gradual addition of a 2 per cent. solution of potassium permanganate. The oxidation was at first very rapid, but afterwards slow, and two days were required before the colour of the permanganate remained. The excess was destroyed by the addition of sodium sulphite, and, after heating to boiling, the filtrate and washings of the manganese precipitate were evaporated to a small bulk. When the solution was acidified, nothing separated, but, after some days, a quantity of a pale yellow, crystalline acid had been deposited, and a further quantity was obtained by extracting the solution with ether. The whole was boiled with water, and thus separated into an insoluble, ochreous substance (A), which was removed by filtration, and an acid which crystallised from the filtrate in sulphur-yellow prisms.

After remaining exposed to the air until quite dry, the acid yielded the following results on analysis:

0.1794 gave 0.3237 CO_2 and 0.0769 H_2O . $\text{C} = 49.1$; $\text{H} = 4.8$.

0.1876 „ 0.3356 CO_2 „ 0.0774 H_2O . $\text{C} = 48.8$; $\text{H} = 4.6$.

$\text{C}_{10}\text{H}_{10}\text{O}_6 \cdot \text{H}_2\text{O}$ requires $\text{C} = 49.2$; $\text{H} = 4.9$ per cent.

This acid, which is doubtless 2:5-*dimethoxyphthalic acid*, melts, or rather decomposes, at about 183 — 186° and contains 1 molecule of water which does not appear to be removed at 90° .

2:5-Dimethoxyphthalic Anhydride.—The ochreous substance (4), insoluble in water and dilute potash, is also very sparingly soluble in all the usual organic solvents, but it dissolves in boiling acetic anhydride, and separates, on cooling, as a bright yellow, crystalline powder, which, under the microscope, is seen to consist of short, glistening prisms not unlike sugar crystals.

0.1430 gave 0.3025 CO_2 and 0.0517 H_2O . $\text{C} = 57.7$; $\text{H} = 4.0$.

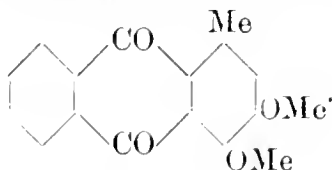
0.1853 „ 0.3884 CO_2 „ 0.0670 H_2O . $\text{C} = 57.4$; $\text{H} = 4.0$.

$\text{C}_{10}\text{H}_8\text{O}_5$ requires $\text{C} = 57.7$; $\text{H} = 3.8$ per cent.

2:5-Dimethoxyphthalic anhydride melts at $260\text{--}261^\circ$, and is characterised by the fact that its dilute solutions, and notably its solution in ethyl acetate, exhibit a magnificent pale blue fluorescence. It dissolves in concentrated sulphuric acid, yielding a pale yellow solution, which has a striking pale green fluorescence like that of uranium glass. Thiele and Günther (*Annalen*, 1906, **349**, 64) have lately obtained 2:5-dimethoxyphthalimide, $(\text{MeO})_2\text{C}_6\text{H}_2\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{NH}$, from dicyanoquinol dimethyl ether, $(\text{MeO})_2\text{C}_6\text{H}_2(\text{CN})_2$, by treatment with sulphuric acid. When this imide was digested with alcoholic hydrogen chloride, it was converted into 2:5-dimethoxyphthalic anhydride, which melted at 259° , and is evidently identical with the anhydride described above. These experiments, together with the observations which we have made, seem to indicate that 2:5-dimethoxyphthalic acid is converted into its anhydride with unusual ease, and, indeed, simply boiling with water seems to bring about this change, at all events partially.

Condensation of Phthalic Anhydride with Dimethylhomocatechol.

Formation of Methylalizarin Dimethyl Ether,



This condensation was carried out by dissolving molecular proportions of phthalic anhydride and dimethylhomocatechol (p. 1649) in light petroleum and gradually adding a quantity of aluminium chloride equal to their combined weights, the whole being well agitated after each addition. When all the aluminium chloride had been added, the mixture was heated on the water-bath for ten hours, and the dark-coloured, viscous aluminium compound was decomposed by ice and hydrochloric acid in the usual manner. The yellow oil, thus obtained, was digested several times with hydrochloric acid, but we were unable

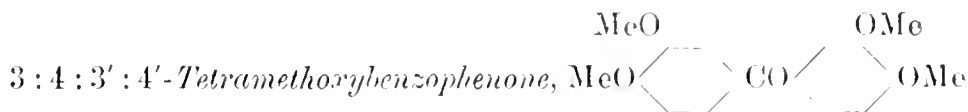
to obtain from it, in a pure state, the dimethoxytoluylbenzoic acid which it undoubtedly contained.

The crude product was next heated with concentrated sulphuric acid at 80° until a drop of the red solution, on dilution with water and treatment with excess of caustic-potash, yielded an insoluble, yellow precipitate. The solution was then poured on ice, the precipitate collected, washed well with water and sodium carbonate, and recrystallised from acetic acid.

0.1634 gave 0.4296 CO_2 and 0.0706 H_2O . $\text{C} = 71.9$; $\text{H} = 4.8$.

$\text{C}_{17}\text{H}_{11}\text{O}_4$ requires $\text{C} = 72.3$; $\text{H} = 4.9$ per cent.

1-Methylalizarin dimethyl ether (1-methyl 3:4-dimethoxyanthraquinone) melts at 224° and is sparingly soluble in benzene, light petroleum, or cold acetic acid; it crystallises from acetic acid in yellow needles and dissolves in sulphuric acid, yielding a brilliant red solution. That this methylalizarin dimethyl ether has the constitution assigned to it at the head of this section can scarcely be doubted, since Lagodzinski (*Ber.*, 1895, 28, 118) has shown that hystazarin dimethyl ether is produced when phthalic anhydride is condensed under similar conditions with veratrole.



[HENRY LEWELLYN SMITH, B.Sc.].

This derivative of benzophenone is readily prepared by condensing veratryl chloride with veratrole in the presence of aluminium chloride.

Veratryl chloride (20 grams) and veratrole (14 grams) are dissolved in carbon disulphide, aluminium chloride (25 grams) is gradually added, and the whole heated on the water-bath for three hours. The product is decomposed by ice and hydrochloric acid and the ketone purified by crystallisation from methyl alcohol.

0.1485 gave 0.3681 CO_2 and 0.0827 H_2O . $\text{C} = 67.6$; $\text{H} = 6.2$.

$\text{C}_{17}\text{H}_{18}\text{O}_5$ requires $\text{C} = 67.6$; $\text{H} = 6.0$ per cent.

The determination of the methoxy-groups by Perkin's modification of Zeisel's method (*Trans.*, 1903, 83, 1367) yielded the following results :

0.1925 gave 0.5667 AgI . $\text{MeO} = 39.0$.

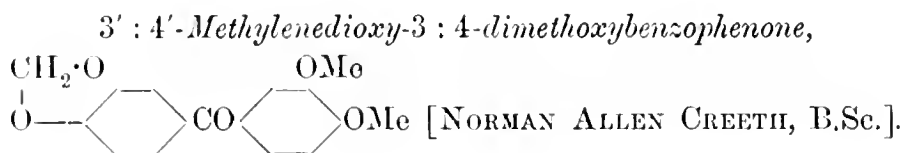
$\text{C}_{17}\text{H}_{18}\text{O}_5$ containing 4MeO requires $\text{MeO} = 41.0$ per cent.

3:4:3':4'-Tetramethoxybenzophenone crystallises from alcohol in colourless needles melting at 144° . It is soluble in benzene and alcohol, less soluble in light petroleum, insoluble in caustic potash.

The *oxime* was prepared by treating the ketone with hydroxylamine hydrochloride and caustic potash in the usual manner. It crystallises from alcohol and melts at 145° .

0.1700 gave 6.6 c.c. nitrogen at 15° and 758 m.m. $N = 4.5$.

$C_{17}H_{19}O_5N$ requires $N = 4.4$ per cent.



This ketone was prepared by mixing piperonyl chloride (18 grams) and resorcinol dimethyl ether (14 grams) in carbon disulphide, adding aluminium chloride (20 grams), and heating on the water-bath for five hours. After decomposing with ice and hydrochloric acid, the ketone was collected at the pump, washed with sodium carbonate, and recrystallised from methyl alcohol. It crystallises in yellow needles, soluble in alcohol, ether, or benzene, less soluble in light petroleum.

0.1827 gave 0.4491 CO_2 and 0.0723 H_2O . $C = 66.9$; $H = 4.4$.

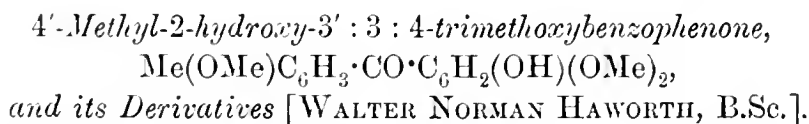
$C_{16}H_{14}O_5$ requires $C = 67.1$; $H = 4.9$ per cent.

The determination of the methoxy-groups gave the following result :

0.2761 gave 0.4100 AgI. $\text{MeO} = 19.6$.

$C_{16}H_{14}O_5$ containing 2MeO requires $\text{MeO} = 20.0$ per cent.

3' : 4'-Methylenedioxy-3 : 4-dimethoxybenzophenone separates from methyl alcohol in pale yellow needles and melts at $141-142^{\circ}$. When treated with hydroxylamine hydrochloride and caustic potash in the usual manner, it yields an oxime which crystallises from methyl alcohol in white crystals, but was not further examined.



The above ketone was obtained by condensing pyrogallol trimethyl ether with the chloride of 2-methoxy-*p*-toluic acid in the presence of aluminium chloride.

The acid chloride (54 grams) and pyrogallol trimethyl ether (50 grams) were finely powdered, suspended in carbon disulphide, and heated on the water-bath with aluminium chloride (56 grams) for about four hours. The product was decomposed by ice and dilute hydrochloric acid, the carbon disulphide removed by di-tillation in steam,

the dark-coloured oil boiled with dilute sodium carbonate, and allowed to stand until it had completely solidified.

The precipitate was collected at the pump and recrystallised from methyl alcohol.

0.1262 gave 0.3135 CO_2 and 0.0691 H_2O . $\text{C} = 67.7$; $\text{H} = 6.1$.

$\text{C}_{17}\text{H}_{18}\text{O}_5$ requires $\text{C} = 67.6$; $\text{H} = 5.9$ per cent.

The determination of the methoxy-groups by Perkin's modification of Zeisel's method gave the following results :

0.1195 gave 0.2746 AgI . $\text{MeO} = 30.4$.

$\text{C}_{17}\text{H}_{18}\text{O}_5$ containing 3 MeO requires $\text{MeO} = 30.8$ per cent.

Methylhydroxytrimethoxybenzophenone melts at 109° and separates from methyl alcohol in long, yellow needles ; it dissolves in caustic potash, and its alcoholic solution gives with ferric chloride a blood-red coloration. These facts prove that the hydrogen chloride evolved during the course of the above reaction had converted one of the MeO groups (obviously that adjacent to the CO group) into the hydroxyl group (compare p. 1655). The yield of ketone obtained from the quantities employed in the above preparation was 20 grams.

4'-Methyl-3' : 2 : 3 : 4-tetramethoxybenzophenone,
 $\text{Me}(\text{OMe})\text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OMe})_3.$

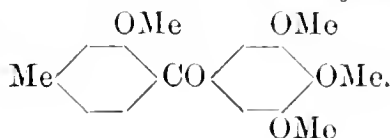
In order to prepare this substance, the methylhydroxytrimethoxybenzophenone just described was dissolved in an excess of aqueous potash (15 per cent.) and well shaken in the cold with an excess of methyl sulphate, when the completely methylated ketone separated as a solid and was purified by recrystallisation from methyl alcohol.

0.1579 gave 0.3951 CO_2 and 0.0900 H_2O . $\text{C} = 68.3$; $\text{H} = 6.4$.

$\text{C}_{18}\text{H}_{20}\text{O}_5$ requires $\text{C} = 68.4$; $\text{H} = 6.3$.

Methyltetramethoxybenzophenone melts at 78° , is insoluble in caustic potash, and gives no coloration when ferric chloride is added to its alcoholic solution.

4'-Methyl-1' : 3 : 4 : 5-tetramethoxybenzophenone,



A derivative of benzophenone, which probably has the above structure, was prepared by condensing *m*-tolyl methyl ether with gallyl

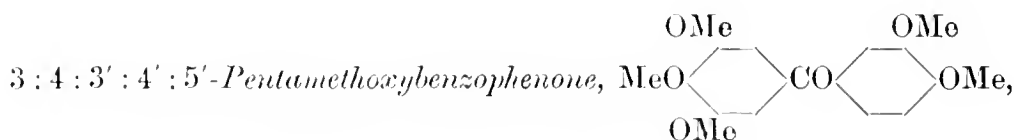
chloride trimethyl ether in the presence of aluminium chloride under the same conditions as those described above.

The product of the reaction consisted of a substance which separated from methyl alcohol in brown plates and melted at 97° .

0.1144 gave 0.2875 CO_2 and 0.0616 H_2O . $\text{C} = 68.5$; $\text{H} = 6.1$.

$\text{C}_{18}\text{H}_{20}\text{O}_5$ requires $\text{C} = 68.4$; $\text{H} = 6.3$ per cent.

This substance is insoluble in caustic potash solution, and therefore the hydrogen chloride formed during its preparation had not, as in two previous cases, converted the methoxy-group adjacent to the carbonyl group into hydroxyl (see pp. 1655, 1663).



and its Derivatives [JONATHAN NAYLOR, B.Sc.].

Gallyl chloride trimethyl ether (23 grams) reacts readily with veratrole (14 grams) when the solution in carbon disulphide is heated on the water-bath with aluminium chloride (23 grams).

The product was treated with ice and dilute hydrochloric acid and the carbon disulphide removed by distillation in steam; the solid ketone was then collected at the pump, washed with sodium carbonate, and purified by crystallisation from methyl alcohol.

0.2002 gave 0.4773 CO_2 and 0.1153 H_2O . $\text{C} = 65.0$; $\text{H} = 6.4$.

$\text{C}_{18}\text{H}_{20}\text{O}_6$ requires $\text{C} = 65.1$; $\text{H} = 6.0$ per cent.

The determination of the methoxy-groups gave the following result:

0.1997 gave 0.6868 AgI . $\text{MeO} = 45.7$.

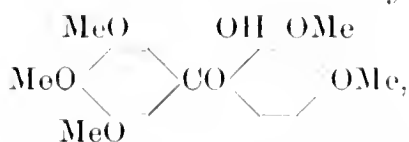
$\text{C}_{18}\text{H}_{20}\text{O}_6$ containing 5 MeO requires $\text{MeO} = 46.7$ per cent.

3:4:3':4':5'-Pentamethoxybenzophenone crystallises from methyl alcohol in pale salmon-coloured crystals and melts at $119-120^{\circ}$. When treated with hydroxylamine hydrochloride and caustic potash in the usual manner, it yields an *oxime* which crystallises from benzene in white needles and melts at 143° .

0.1666 gave 6.3 c.c. nitrogen at 16° and 758 mm. $\text{N} = 4.4$.

$\text{C}_{15}\text{H}_{21}\text{O}_6\text{N}$ requires $\text{N} = 4.0$ per cent.

2-Hydroxy-3 : 4 : 3' : 4' : 5'-Pentamethoxybenzophenone,



and its Derivatives [VICTOR JOHN HARDING, B.Sc.].

In preparing this derivative of benzophenone, gallyl chloride trimethyl ether (39 grams) was mixed with pyrogallol trimethyl ether (31 grams) and heated in carbon disulphide solution on the water-bath with aluminium chloride (30 grams) in the manner already described (p. 1664). The ketone was purified by recrystallisation from methyl alcohol.

0.1447 gave 0.3290 CO₂ and 0.0734 H₂O. C = 62.0; H = 5.6.

0.1661 „ 0.3748 CO₂ „ 0.0820 H₂O. C = 62.1; H = 5.5.

C₁₈H₂₀O₇ requires C = 62.1; H = 5.7 per cent.

2-Hydroxy-3 : 4 : 3' : 4' : 5'-pentamethoxybenzophenone melts at 133—134°, dissolves in dilute potash with an intense yellow colour, and the solution in alcohol gives with ferric chloride an intense blood-red coloration. These properties prove that the substance contains a hydroxyl group, the presence of which is due to the action of the hydrogen chloride produced in the above condensation: the position of this hydroxyl group is doubtless that shown in the formula at the head of this section.

The *oxime*, prepared by the action of hydroxylamine hydrochloride and caustic potash in the usual manner, separates from alcohol in feathery crystals and melts at 178—179°.

0.1609 gave 6.2 c.c. nitrogen at 15° and 752 mm. N = 4.4.

C₁₈H₂₁O₇N requires N = 3.9 per cent.

2 : 3 : 4 : 3' : 4' : 5'-Hexamethoxybenzophenone is produced when hydroxypentamethoxybenzophenone is treated with aqueous caustic potash and methyl sulphate (p. 1663).

It melts at 121°, crystallises from methyl alcohol in glistening prisms, is insoluble in caustic potash, and gives no coloration when ferric chloride is added to its alcoholic solution.

0.1867 gave 0.4306 CO₂ and 0.0971 H₂O. C = 62.9; H = 5.8.

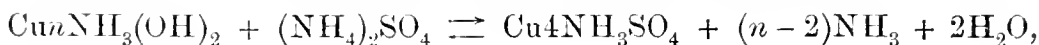
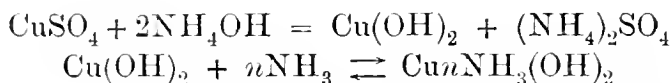
C₁₉H₂₂O₇ requires C = 63.0; H = 6.1 per cent.

THE UNIVERSITY,
MANCHESTER.

CLXVII.—*The Nature of Ammoniacal Copper Solutions.*

HARRY MEDFORTH DAWSON.

IN two previous papers (Dawson and McCrae, *Trans.*, 1900, **77**, 1239 ; 1901, **79**, 1072) experimental data have been recorded which tend to throw some light on the nature of aqueous solutions of certain metal-ammonia compounds. In the former paper ammoniacal solutions of copper, zinc, cadmium and nickel salts were investigated and the conclusion was drawn that these metals form ammonia compounds of the same type. The method of investigation employed consisted in measuring the total and free ammonia in the ammoniacal solutions. The free ammonia was determined by measuring the amount extracted when the solutions were shaken up with chloroform at a definite temperature. The molecular ratio of combined ammonia to metal was found to vary between 3.15 and 4.0. For a given concentration of the metallic salts the ratio was found to increase with the quantity of ammonia present, and with a fixed proportion of total ammonia to metal, the molecular ratio of combined ammonia was found to increase with the absolute concentration. Dissociation phenomena were thus indicated by the experimental data, and it was suggested that the changes which take place when ammonia is gradually added to a solution of one of these salts (for example, copper sulphate) might be represented by the scheme :



n being less than 4 and probably equal to 2.*

According to this scheme the ammoniacal solution of copper sulphate represents a complex system, in which the copper is present in the form of three different ions, $\text{Cu}4\dot{\text{N}}\text{H}_3$, $\text{Cu}n\dot{\text{N}}\text{H}_3$, and $\dot{\text{Cu}}$, the relative proportions of these depending upon the concentration of the solution and the relative proportions of ammonia and copper salt.

Since the publication of these results, Locke and Forssall (*Amer. Chem., J.*, 1904, **31**, 268) have investigated ammoniacal solutions of copper sulphate, and arrived at the conclusion that the copper in such solutions is almost entirely present in the form of a very stable ion, $\text{Cu}4\dot{\text{N}}\text{H}_3$. The differences in the value of the molecular ratio of

* The value of n , previously supposed equal to 2, will not be discussed in this paper.

combined ammonia to copper with varying concentration of the solutions as found by McCrae and myself, are stated to be due to the fact that the method employed by us does not give the correct values for the concentration of free ammonia in the solutions. The experimental method of Locke and Forssall, which consisted in passing a current of electrolytic gas through a column of the solution immersed in a thermostat, and measuring the amount of ammonia removed by a known volume of the gas, does not, however, differ essentially from the mode of examination adopted by us.* It is precisely on this account that the conclusions deduced from the two series of experimental data might be expected to agree. Locke and Forssall, however, found that the molecular ratio of combined ammonia to copper is constant, and independent of the total ammonia concentration, and this, they point out, is not consistent with the view that more than one complex copper compound is present in the solution. The fact that the experimentally determined values of the ratio $\text{NH}_3 : \text{Cu}$ are considerably smaller than four, as required by the complex ion $\text{Cu}_4\ddot{\text{N}}\text{H}_3$, is supposed to be entirely due to the smaller solubility of ammonia in ammoniacal copper solutions as compared with pure water. Not only is this assumption made, but from the difference between the required molecular ratio and that actually found in the case of the least concentrated copper solution examined, a measure of the decrease in the solubility is deduced. By means of the empirical formula suggested by Jahn (*Zeit. physikal. Chem.*, 1895, 18, 8), to express the influence of concentration on the lowering of the solubility of certain gases in water on the addition of electrolytes, values are then deduced as correction factors for the two more concentrated solutions examined. The actual values recorded by these authors for the constant molecular ratio $\text{NH}_3 : \text{Cu}$ are 4.03, 3.98 and 3.95 for 0.0235, 0.0470 and 0.1175 molecular copper solutions respectively.

The conclusions drawn from numbers so obtained can, obviously, not be accepted. The value of the correction introduced for the diminished solubility of ammonia in the copper solutions is, in the first instance, perfectly arbitrary, and the application of Jahn's formula to solutions of ammonia is not justified by any experimental evidence.†

* It may be noted that, according to Carveth and Fowler (*J. Physical Chem.*, 1904, 8, 313), exact measurements of vapour pressure cannot be at all readily obtained by the method of air bubbling. On the other hand, Perman (*ibid.*, 1905, 9, 36) asserts that the method yields accurate results.

† More recent experiments have led to the setting up of other formulæ to express the influence of electrolytes on the solubility of non-electrolytes in water (compare Rothmund, *Zeit. physikal. Chem.*, 1900, 33, 401; Euler, *ibid.*, 1904, 49, 303; Dawson and McCrae, *Trans.*, 1901, 79, 493).

The purely experimental results obtained by Locke and Forssall appeared, however, to warrant a further inquiry into the matter, and the present investigation has been instituted with this object. In the first paper by McCrae and the author (*loc. cit.*) the primary object was to obtain a general survey of the nature of the ammoniacal solutions and to compare the behaviour of different metals rather than to ascertain with the maximum degree of accuracy the phenomena in the case of any particular metal. The experiments described in this paper, however, represent an attempt to elucidate the nature of ammoniacal solutions of copper sulphate as accurately as is possible by the method of examination employed.

The actual experimental work was carried out in the manner previously described, but in order to obtain greater accuracy, especially in the case of the more dilute solutions, much larger quantities of aqueous solution and of chloroform were employed, and the thermostat, in which the experiments were made, was so arranged that the temperature variations did not exceed $\pm 0.025^\circ$.

In reference to the distribution of ammonia between pure water and chloroform, it has already been shown that the concentration ratio $c_{\text{H}_2\text{O}}/c_{\text{CHCl}_3}$ decreases with increasing ammonia concentration, but the relationship between these two factors could not be determined with a desirable degree of accuracy in the case of dilute solutions containing less than 0.5 mol. of ammonia per litre of aqueous solution. On this account, further measurements have been made according to the improved experimental method. The data are collected in Table I; c and c' denote the molar concentration of ammonia in water and chloroform respectively, and k the distribution ratio $= c/c'$. The temperature at which all experiments were made was 19.5° .

TABLE I.

c	0.1540	0.1885	0.2011	0.2074	0.3336	0.3958	0.4898
c'	0.005919	0.007283	0.007759	0.008028	0.01299	0.01545	0.01923
k	26.01	25.87	25.92	25.83	25.67	25.61	25.46
c	0.5207	0.6247	0.6674	0.7551	0.8796		
c'	0.02043	0.02463	0.02646	0.03005	0.03522		
k	25.49	25.36	25.23	25.14	24.98		

If the values of k are graphically represented as a function of c' , the points so obtained lie very approximately on the straight line corresponding to the equation :

$$k = 26.16 - 34.14 c' \dots \dots \dots (1)$$

The supposed deviations from this linear relationship, indicated by the earlier experiments at small ammonia-concentrations, are not confirmed by these more accurate measurements.

Before a knowledge of the ratio of distribution of ammonia between water and chloroform can be utilised to determine accurately the quantity of free ammonia in ammoniacal solutions of copper sulphate several points require consideration. Firstly, water and chloroform represent a pair of liquids which at the ordinary temperature are slightly miscible. According to Herz (*Ber.*, 1898, 31, 2669), at 22°, 100 c.c. of water dissolve 0.429 c.c. of chloroform and give 100.39 c.c. of solution, whilst 100 c.c. of chloroform dissolve 0.152 c.c. of water and the volume of the solution is 99.62 c.c. The extent of this mutual solubility is no doubt altered when ammonia is present in the two liquids and copper salt in the water. Secondly, when a copper sulphate solution of definite concentration is shaken up with chloroform, this concentration will undergo a slight change, the amount of which depends at a given temperature on the original concentration and on the relative volumes of the solution and of chloroform which are brought together. In ammoniacal solutions the change of concentration from this cause will also no doubt depend on the ammonia concentration. This change of concentration cannot be directly ascertained from the data which measure the miscibility of pure water and pure chloroform, for the mutual solubility is altered by the presence of the foreign substances (ammonia and copper salt) in the two liquids. Thirdly, the influence which the dissolved copper compound (or compounds) exerts on the distribution of the free ammonia between water and chloroform must be taken into account. This influence is no doubt very considerable and an accurate knowledge of it is necessary for the determination of the true values of the combined ammonia, but its magnitude cannot be determined by direct experiment. On the basis of the numerous data already obtained for salts of the alkali metals (Dawson and McCrae, *Trans.*, 1901, 79, 493), it may be inferred, however, that the direction of this influence is such that the relative solubility of the free ammonia in the water is diminished. In the case of these salts, it is improbable that the effect of the dissolved electrolyte is complicated to any appreciable extent by chemical interaction with the ammonia. The magnitude of the influence is dependent on the nature of the component ions and is additive in character. The carbonates, sulphates, and oxalates are much more active than the iodides, bromides, and nitrates of the same metal.

The experimental method, having regard to the first two disturbing factors, may now be considered. If the relative volumes of water and chloroform are suitably chosen, the volume of the aqueous solution will not be altered after shaking with chloroform. Utilising Herz's data, it can be easily shown that the volume of chloroform which must be shaken up with 100 c.c. of water, in order that this condition

may be satisfied, is given by the equation: $x = \frac{100}{0.152} \left(100 - \frac{(100)^2}{100.39} \right)$, from which $x = 256$ c.c. If we assume that the ammonia and copper salt do not appreciably affect the mutual solubility of the two liquids, it follows that, by employing ammoniacal copper solutions and chloroform in the volume ratio 1:2.56, the concentration of the dissolved copper will be unchanged. This conclusion and the somewhat arbitrary assumption involved were submitted to the test of experiment. Sixty c.c. of an ammoniacal copper sulphate solution ($\text{NH}_3 = 1.00$ ($\text{Cu} = 0.0501$ mol. per litre) were shaken up with 150 c.c. of chloroform and the resulting aqueous solution was found to contain 0.0502 mol. Cu per litre. The concentration of the dissolved copper is evidently unaltered in these circumstances, and in the experiments to be described the relative volumes were chosen in accordance with this condition.

In respect of the third disturbing factor, it has already been found that the influence of alkali salts on the ammonia distribution is proportional to their concentration. This proportionality has been confirmed by a new series of more accurate experiments with sodium sulphate. In these experiments, the ammonia concentration in the chloroform was very nearly constant and equal to 0.015 mol. per litre, for which concentration the distribution ratio in the case of pure water k is equal to 25.64. In the table, the sodium sulphate (m) and ammonia (c and c') concentrations in mol. per litre are given in the first, second, and third columns; the fourth contains the values of the distribution ratio k' , the fifth the values of $(k - k')/m$. For the purpose of comparison, the values of $k - k'/m^{\frac{2}{3}}$ are also given.

TABLE II.

m .	c (H_2O).	c' (CHCl_3).	k' .	$k - k'/m$.	$k - k'/m^{\frac{2}{3}}$.
0.156	0.3694	0.01534	24.07	10.05	5.41
0.313	0.3411	0.01512	22.56	9.84	6.68
0.469	0.3196	0.01512	21.13	9.62	7.47

The values of $k - k'/m$ are very nearly constant and indicate that the "salting-out" effect is very approximately proportional to the concentration of the dissolved salt, and not to the (concentration) $^{\frac{2}{3}}$ as was gratuitously assumed by Locke and Forssall in the case of the vapour pressure.

In a second series of experiments the concentration of the sodium sulphate was in every case 0.313 mol. per litre, whilst the ammonia concentration was varied.

TABLE III.

c (H_2O).	c' (CHCl_3).	k (from equation 1).	k' .	$k - k'/m$.
0.1755	0.007668	25.90	22.88	9.65
0.3111	0.01512	25.61	22.56	9.81
0.6513	0.02956	25.15	22.11	9.62

The numbers indicate that the "salting out" action of the sodium sulphate is independent of the ammonia concentration within the limits of concentration employed.

On the basis of these experimental results the distribution ratio k' of ammonia between an aqueous solution of an electrolyte and chloroform may be expressed by the equation :

$$k' = k - \delta m = 26.16 - 34.14 \ c' - \delta m \dots \dots \dots (2)$$

in which c' is the ammonia concentration in the chloroform, m the concentration of the electrolyte in the aqueous solution, and δ the "salting-out" effect produced by the electrolyte at a concentration of 1 mol. per litre.

By means of this equation the concentration of the free ammonia in an aqueous solution of the electrolyte can be determined, and if the total ammonia concentration is known, the combined ammonia is given by the difference. For the molecular proportion of combined ammonia in an ammoniacal copper solution, we have then

$$\text{Mol. ratio } \frac{\text{Combined NH}_3}{\text{Cu}} = \frac{c - k'c'}{m} = \frac{c - kc'}{m} + \delta c' \dots \dots (3)$$

The value of δ , which measures the "salting-out" or ammonia displacing effect of the dissolved cupriammonia compound, is, of course, unknown, but the calculation of the combined ammonia may be carried out with two limiting values of δ , such that the true value is in all probability intermediate. As a lower limit $\delta = 0$ has been taken, and as a higher limit $\delta = 10$, which is the value found in the case of sodium sulphate, and represents an ammonia displacing power of considerable magnitude.

Before the experimental numbers are communicated, it may be noted that, according to equation (3), the measurement of the combined ammonia depends on the difference between two quantities, both of which increase with increasing total ammonia concentration. For this reason the accurate determination of combined ammonia in the case of solutions containing considerable excess of ammonia is impracticable. On the other hand, the concentration of ammonia in the chloroform is so small in the case of aqueous solutions containing little free ammonia

that a limit to the accurate experimental determination of combined ammonia is also fixed in this direction. These considerations have determined the limits of the investigation which on general grounds has been confined to dilute solutions.

Four series of experiments have been carried out in which the concentration of the copper salt was respectively 0.0125, 0.025, 0.05, and 0.10 mol. per litre. In each of these series the ammonia concentration was varied, the extreme values for the molecular ratio $\text{NH}_3:\text{Cu}$ being 5.5 and 24. In most cases, the experiments were made in duplicate. In the table the successive columns contain (1) the ammonia concentration of the aqueous solution in mols. per litre, (2) the molecular ratio of total ammonia to copper, (3) the ammonia concentration of the chloroform solution, (4) the distribution ratio k calculated from equation (1), and (5) the molecular ratio of combined ammonia to copper calculated for $\delta=0$ and $\delta=10$ according to equation (3).

TABLE IV.

Concentration of Copper, 0.0125 mol. per litre.

$\text{NH}_3(\text{H}_2\text{O})$.	Mol. ratio, total NH_3/Cu .	$\text{NH}_3(\text{CHCl}_3)$.	k .	Mol. ratio, Combined NH_3/Cu .	
				$\delta=0$.	$\delta=10$.
0.1042	8.34	0.002438	26.08	3.25	3.27
0.1055	8.44	0.002479	26.08	3.27	3.29
0.1975	15.80	0.005940	25.96	3.46	3.52
0.2001	16.01	0.006040	25.96	3.46	3.52
0.2981	23.84	0.009860	25.82	3.46	3.56

Concentration of Copper, 0.025 mol. per litre.

0.1754	7.02	0.00347	26.04	3.40	3.43
0.1776	7.10	0.00358	26.04	3.37	3.41
0.2169	8.68	0.00500	25.99	3.48	3.53
0.2177	8.71	0.00502	25.99	3.49	3.54
0.3799	15.20	0.01121	25.78	3.64	3.75
0.3800	15.20	0.01123	25.78	3.62	3.73

Concentration of Copper, 0.05 mol. per litre.

0.3042	6.08	0.00492	25.99	3.53	3.58
0.3367	6.73	0.00613	25.95	3.55	3.61
0.3370	6.74	0.00616	25.95	3.54	3.60
0.5572	11.14	0.01466	25.66	3.62	3.77
0.5590	11.18	0.01463	25.66	3.67	3.82
0.5964	11.93	0.01605	25.61	3.70	3.86
0.8521	17.04	0.02658	25.25	3.61	3.88

Concentration of Copper, 0.10 mol. per litre.

0.5476	5.48	0.00711	25.92	3.64	3.71
0.5486	5.49	0.00710	25.92	3.65	3.72
0.9488	9.49	0.02275	25.38	3.71	3.94
0.9605	9.60	0.02315	25.37	3.73	3.96

In regard to the two series of numbers in column (5), it is to be noted that the true values of the combined ammonia are in all probability intermediate to the two values given. Although the true values are not determinable by the experimental method employed in this investigation, yet the numbers indicate with certainty that, for a given copper concentration, the molecular ratio of combined ammonia to copper increases with increase in the total ammonia concentration. The variation of the proportion of combined ammonia for a given alteration in the ammonia concentration is evidently greater when the ammonia displacing influence of the dissolved complex compound is taken into account in the calculation.

The following numbers, which are interpolated from the data in the previous table, show the variation of the proportion of combined ammonia with the concentration of the solution when the ratio of total ammonia to copper is kept constant.

TABLE V.

Concentration of copper salt, mol. per litre.	Mol. ratio, total NH_3/Cu .	Mol. ratio, combined NH_3/Cu .	
		$\delta = 0$.	$\delta = 10$.
0.0125	8.0	3.25	3.27
0.025	8.0	3.43	3.49
0.05	8.0	3.58	3.67
0.10	8.0	3.69	3.86

It is clear that with increasing dilution the proportion of combined ammonia decreases to a considerable extent, and the variation is greater when it is assumed that $\delta = 10$ than when $\delta = 0$.

Some experiments carried out with solutions of the crystalline salt, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, may now be described. The cupriammonia sulphate was prepared according to the method described by André (*Compt. rend.*, 1885, 100, 1138) by passing ammonia into a concentrated and well-cooled solution of copper sulphate, washing the separated crystals with aqueous ammonia and drying over lime. Analysis of the crystals gave $\text{Cu} = 25.85$, $\text{NH}_3 = 27.86$, the formula requiring $\text{Cu} = 25.85$ and $\text{NH}_3 = 27.76$ per cent.

Concentrated solutions of this salt appear to be quite stable, but on dilution precipitation takes place. A freshly-prepared solution containing approximately 0.1 mol. per litre appears to be optically clear, but care must be taken in the preparation of the solution if the formation of a precipitate is to be avoided. On standing for some days, a portion of the copper is precipitated from such a solution. It was of some interest to determine the proportion of combined ammonia in these solutions, and two freshly-prepared approximately 0.1 molar

solutions were examined, the data obtained being given in the following table. In the case of the second solution, the copper concentration was determined both before and after shaking with chloroform. The difference in the two values indicates that a small proportion of the copper was removed from the aqueous solution by the process of extracting with chloroform, and it is possible that this represents copper already present in the form of colloidal or suspended copper hydroxide. In the interpretation of the experimental data, this possibility must be kept in mind.

TABLE VI.

Copper concentration.	$\text{NH}_3 (\text{H}_2\text{O}).$	$\text{NH}_3 (\text{CHCl}_3).$	Mol. ratio, combined $\text{NH}_3/\text{Cu}.$	
			$\delta=0.$	$\delta=10.$
0.1021	0.4044	0.001995	3.45	3.47
(0.0990 (before expt.)	0.3918	0.00210	3.40	3.42
(0.0985 (after ,,)	0.3918	0.00210	3.42	3.44

The values of the ratio of combined ammonia to copper indicate that an aqueous solution of the substance $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ contains a considerable quantity of free ammonia resulting from the dissociation of the complex compound, and the data agree satisfactorily with those obtained in the examination of solutions containing larger quantities of ammonia.

The observations recorded in this paper lead the author to conclude that the view of Locke and Forssall, according to which ammoniacal solutions of copper sulphate contain copper exclusively in the form of a stable complex ion, $\text{Cu} \cdot 4\ddot{\text{N}}\text{H}_3$, is untenable.

In concentrated solutions or solutions containing considerable excess of ammonia, the copper appears to be present very largely in the form of this ion, but on dilution of the solution or decrease in the relative proportion of the ammonia, this complex ion undergoes dissociation with the separation of ammonia, the process leading ultimately to the precipitation of copper hydroxide from solution. Although the exact nature of the changes is not yet known, yet the experimental facts are in agreement with the equations on p. 1666. It is hoped that experiments which are in progress will throw further light on the nature of this complex system.

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CLXVIII.—*A Development of the Atomic Theory which Correlates Chemical and Crystalline Structure and leads to a Demonstration of the Nature of Valency.*

By WILLIAM BARLOW and WILLIAM JACKSON POPE.

THE morphotropic relationships observed between related chemical substances, fragmentary as they are, indicate convincingly that crystal structure is a function of chemical constitution, although no satisfactory suggestion as to the nature of this function has yet been made. Further, the simple character and wide applicability of the doctrine of valency suggests that valency is capable of a perfectly definite physical interpretation; the failure of the numerous attempts which have been made to convert the doctrine of valency into a concept comparable in definiteness with the atomic theory does not weaken the conviction as to its possibility.

The determination of the nature of valency and of the connexion existing between chemical constitution and crystal form is a problem affecting the foundations of both chemistry and crystallography. By adopting a very simple fundamental conception as to the nature of the environment of the atoms in a chemical molecule which will be acceptable to the chemist and applying to it methods of treatment which will be acceptable to both crystallographer and chemist, we find ourselves able to offer a scheme, which, whilst in entire harmony with current views of molecular constitution, indicates quantitatively the relation of chemical constitution and crystalline form for any compound substance, and interprets valency as a simple volume relation.

The fundamental conception which forms the basis of the present work is briefly stated below, and this statement is followed by a discussion in which the conception is expanded or developed into a form susceptible of treatment by the geometrical methods of crystallography.

The Fundamental Conception.

Each chemical atom present in a compound occupies a distinct portion of space by virtue of an influence which it exerts uniformly in every direction. The domain of a chemical molecule is the space-unit consisting of one or more of these distinct portions of space, obtained by homogeneously sub-dividing into units a homogeneous structure built up of the spheres of influence of a number of associated atoms. The form of aggregation of the spheres of influence of the atoms thus

associated in a molecule constitutes the stereometric arrangement of these atoms and thus the chemical molecule acquires a definite shape. A crystal is the homogeneous structure derived by the symmetrical arrangement in space of an indefinitely large number of spheres of atomic influence.*

Development of the Fundamental Conception.

A mechanical assemblage of the nature contemplated by the above fundamental conception may be a stable one if subject to the operation of two opposing influences acting between the atomic centres, namely, (1) a repellent force, which may be attributed to the kinetic energy of the atoms, (2) an attractive force of the nature of gravity. The simplest premise is that these, and no other opposing forces, are operative. The nature of the equilibrium in such an assemblage is represented by the hypothesis that space is filled by spheres of atomic influence which are in mutual contact at their boundaries; for most practical purposes it suffices to regard the assemblage as in static equilibrium under the influence of the two opposing forces, although the spheres of atomic influence are doubtless the seat of considerable activity of movement.

It is noteworthy that the assumption of simultaneously operative attractive and repulsive forces acting between the atoms has been made in every serious attempt to visualise atomic and molecular action. Boscovich in 1758 premised that the atoms are held apart and at equilibrium distances as the result of an equilibrium established between the attractive and repulsive forces acting between them; by postulating the existence of similar forces acting between the molecules of gases and liquids, van der Waals has more recently succeeded in accounting almost perfectly for the physical behaviour of fluids. The conclusion that the atoms appropriate distinct and characteristic portions of space in the manner now premised has been rendered unquestionable by the unique comparative work of Tutton on the alkali sulphates and double sulphates and the corresponding selenates. (Compare also Sollas, *Proc. Roy. Soc.*, 1898, **63**, 271.)

The attractive forces acting between the atoms will cause the portions of space which they respectively appropriate, supposed as spherical as possible, to be in contact one with another, at the

* The meaning attached to the term "homogeneous" in the present paper is indicated by the following definition: a homogeneous structure or assemblage is one in which every point or unit possesses an environment identical with that of an infinitely large number of other similar points or units in the assemblage if the latter is regarded as indefinitely extended throughout space (compare Barlow, *Min. Mag.*, 1897, **11**, 120; *Sci. Proc. Roy. Dubl. Soc.*, 1897, **8**, 528).

maximum number of points; and as a result of this the atoms composing a chemical molecule will lie as closely together as possible whilst the molecules themselves will also pack closely together into the minimum compass. In other words, the spheres of influence of the atoms composing a molecule will be forced into such relative positions as will permit of the molecules themselves packing together closely. The total effect produced is thus one corresponding to that of a uniform compression exerted upon a concourse of elastic bodies in contact, the necessary result of which would be to leave a minimum of interstitial space.

Now the maximum closeness of packing of a number of similar bodies is commonly attained in some homogeneous arrangement of them, that is, in some arrangement in which the distribution of the structural units is the same about every unit. And, since all crystalline structures are homogeneous assemblages built up of certain units, which units we conceive to be the chemical molecules, we develop from our fundamental conception the view that a crystalline structure is a close-packed, homogeneous assemblage of the spheres of influence of the component atoms.

The close-packed, homogeneous assemblage of spheres of atomic influence derived by the comparatively simple process of development just indicated is partitionable, homogeneously, into cells which are all exactly similar and each of which contains a chemical molecule. The essential feature of the new method of investigation introduced in the present paper is the formation of close-packed assemblages corresponding to different chemical compounds and the study of the partitionings of them which can be effected. Inasmuch as the close-packed assemblage must coincide in symmetry and relative dimensions with the crystalline structure of the substance represented, our method may be checked to a large extent quantitatively by reference to the crystallographic measurements; and since the assemblage itself can be partitioned into units identical in composition, configuration, and shape with the chemical molecule, the study of this partitioning at once reveals a number of important geometrical properties of the molecule. Many of these properties furnish immediate explanations of observed peculiarities of chemical behaviour, such as those relating to tautomeric or isodynamic compounds, to substitution in aromatic nuclei, and the like. In the present work, the necessity never arises for introducing the common conception that, within the molecule, the portions of space appertaining to different atoms overlap—that, like figure-skaters associated in the production of some complex figure, the different atoms follow paths which cross or interweave—and thereby give rise to tautomerism and intermolecular change. Further, the ambit of this inquiry does not involve the assumption that the

individual atoms possess polarity, although the derived cluster or molecule may, and indeed often does, exhibit polarity as a consequence of the arrangement of the atoms.

The construction of close-packed assemblages representing molecular complexes by the packing together of the spheres of atomic influence of various elements naturally involves the assignment of specific volumes or diameters to the latter. It might therefore seem at first sight that fresh assumptions defining these volumes are necessary, and that these would be as axiomatic in character as is our fundamental conception; this, however, is not the case, and for a reason which will be fully developed later, but which may be indicated briefly here.

On studying the methods by which one close-packed homogeneous assemblage of spheres may be converted, geometrically, by substitution of certain of its parts, into related close-packed homogeneous assemblages, geometrical properties governing the substitution become revealed which are of perfectly general applicability and which lead at once to a geometrical interpretation of valency. These geometrical properties are discussed later, but one must be noted here. It is that if some set of spheres in the assemblage is to be replaced by another set which is to occupy the same cavities, and in such a way that the new and also homogeneous assemblage shall retain the same general arrangement of parts and the same density of packing as the old one, the total solid volume of the substituting and substituted spheres must be almost the same. Thus, for instance, in the close-packed homogeneous assemblage representing benzene, groups are found of three hydrogen spheres, one of the three spheres belonging to each of three adjacent molecules; if one-sixth of these groups are to be symmetrically replaced each by one nitrogen sphere, so as to produce the assemblage for triphenylamine, the sphere representing nitrogen must have about three times the volume of that representing hydrogen. If these relative volumes are chosen, the replacement can be effected so that close-packing and homogeneity are retained practically unimpaired; if other relative volumes are assigned to the spheres representing nitrogen and hydrogen, the derived assemblage cannot be rendered homogeneous and as close-packed as before without such a re-arrangement of its parts that it no longer represents chemically the triphenyl derivative of ammonia.

The ordinary law of valency is thus merely an interpretation of a simple geometrical property of close-packed homogeneous assemblages of spheres; the other aspects of valency, such as multivalency, the valency of compound radicles, etc., are, as will appear later, also directly traceable to simple geometrical properties of such assemblages.

To prevent misunderstanding, three remarks must at once be made concerning this application of geometrical principles. First, it is not to be supposed that the whole numbers by which we ordinarily represent the valency of the different elements stand precisely in the ratios of the volumes of the spheres of atomic influence; these numbers are merely approximations and the spheres of atomic influence of the univalent elements, for instance, are not quite the same. Indeed, peculiarities in the types of combination occurring between allied elements of the same valency may be traced to slight deviations from this geometrical interpretation of the valency numbers. Secondly, the volume ratios of the spheres of influence of different elements do not remain quite constant under changes of condition; thus, differences exhibited between the types of combination effected between two given elements at different temperatures may be traced to slight differences in the relative rate of increase of the volumes of the atomic spheres of influence as the temperature rises. Thirdly, in passing from compound to compound, the absolute magnitudes of the spheres of atomic influence often change considerably, although the relative magnitudes are but slightly affected.

These three remarks are not the direct outcome of the fundamental conception, but are the result of a consideration of the observed facts in the light of that conception. The third is of importance in connexion with the theory of molecular volumes, in that it indicates that the molecular volume is not an additive property which can be summed up from component atomic volumes in the simple manner attempted in the past. An example which will make this clear may be drawn from the data (p. 1699) relating to benzene and its derivatives containing halogen. It is there shown that, taking the spheres of atomic influence of carbon as of volume four, those of hydrogen, chlorine, and bromine, as of volume one, benzene and its per-halogen derivatives are characterised by presenting an almost identical spatial arrangement of the component spheres of atomic influence. Now this could not be the case if the atoms of carbon, hydrogen, chlorine, and bromine, in these compounds actually appropriated respectively the atomic volumes 11.0, 5.5, 22.8, and 27.8 stated by Kopp. The interpretation of the evidence adopted in this paper is that in benzene of molecular volume 77.4 and tetrabromobenzene of molecular volume 130.2, the sphere of influence of the carbon atom is about four times as large as those of either hydrogen or bromine; but that on introducing the bromine atoms into the benzene molecule the volumes of the spheres of influence of both carbon and hydrogen expand proportionally in the ratio of 77.4:130.2 (compare Thorpe, *Trans.*, 1893, 63, 811).

The rational character of the conclusion now drawn is well illus-

trated by the axial ratios and molecular volumes of potassium and caesium sulphates (Tutton, Trans., 1905, 87, 1188).

K_2SO_4	Mol. vol. = 64.91.	$a : b : c = 0.5727 : 1 : 0.7418$.
Cs_2SO_4	,, = 84.58.	$a : b : c = 0.5712 : 1 : 0.7531$.

It will be seen that in passing from potassium to caesium sulphate the molecular volume increases by about one-third, whilst the axial ratios remain almost unchanged; it is inconceivable that this close adherence to the type would survive a large increase in size of only one constituent atom of the molecule, but if, as we now conclude, the substitution of caesium for potassium merely expands the whole molecule uniformly from the volume 64.91 to 84.58, the spheres of influence of the atoms of different valency preserving the same ratios, the retention of the original crystalline structure would be expected.

During recent years much attention has been devoted to the study of the so-called "topic axial ratios" of crystalline substances, these values being calculated in the most general case of an anorthic substance from the axial ratios, $a : b : c$, the interaxial angles, α , β , and γ , and the molecular volume, V , by means of the formulæ,

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \alpha \sin \beta \sin \gamma}}, \quad \psi = \chi' a, \text{ and } \omega = c\psi.$$

If proper axial directions are selected, and if proper multiples of the axial ratios are used in calculating the topic axial ratios, a' , b' , and c' , and a'' , b'' , and c'' of two comparable substances, the ratios $a' : a''$, $b' : b''$, and $c' : c''$, represent the relative distances at which the units of the structures are distributed in space in the three axial directions, a , b , and c , respectively. The topic axial ratios, however, have no significance which assists in the detection of relationships between crystalline form and molecular constitution; and it is for this reason that their study has hitherto afforded no information on the subject which could not have been equally well derived from the consideration of the ordinary axial ratios.

For our present purpose, it is of service to learn for series of crystalline substances the dimensions of the molecule in three properly selected axial directions and its volume in terms of the dimensions and volume of the valency unit, which consists of the portion of space allotted to a univalent atom present in the molecule, half that occupied by a bivalent atom, one-third that occupied by a trivalent atom, &c. The volume occupied by the molecule, which is the sum of the volumes of the component spheres of atomic influence, may thus be taken as the sum of the valencies of the component atoms; this sum of the valencies we term the valency volume, W . The valency volume

thus derived involves the assumption that the spheres of atomic influence fill space without interstices.

The molecular dimensions referred to are given by the "equivalence parameters," x , y , and z , calculated in the following manner from the axial ratios and the valency volume.

$$x = \sqrt[3]{\frac{a^2 W}{c \sin \alpha \sin \beta \sin \gamma}}, \quad y = x/a, \text{ and } z = cy.$$

The equivalence parameters are naturally the products of the corresponding topic axial ratios by $3 \sqrt{(W/V)}$.*

The axial directions to which crystalline substances are ordinarily referred for descriptive purposes are not, in general, directions along which occur the minimum distances separating the centres of the structural units. Thus, one important type of cubic crystalline substances is that in which the centre points of the structural units lie at both centres and angles of a cubic partitioning of space, and in this system the distance separating centres of structural units is a minimum along the trigonal axes, this separating distance being $\sqrt{3}/2$ of that along the rectangular cubic axes ordinarily used. If, therefore, the topic axial ratios or the equivalence parameters are to express the minimum distances separating centres of structural units in the crystal, they must be stated with relation to the appropriately selected directions in which those minimum distances occur; in the particular cubic system instanced above, the directions to be selected would be

* For the information of non-crystallographic readers, it may be stated that crystalline substances are classified according to their symmetry in six systems, which are themselves subdivided into thirty-two crystal classes. A crystalline substance is characterised, first, by its symmetry, or the crystal class to which it belongs, and, second, by stating the ratio $a:b:c$ between the lengths of the three edges of a parallelepipedal figure from which the crystal structure may be regarded as built up; the angles bc , ac , and ab , between the axial directions a , b , and c , are termed α , β , and γ . Certain of these constants are, in general, fixed by the symmetry of the crystal system, and the appended list states the crystal systems in order of symmetry and those constants (marked ?) which are not defined by the symmetry and which therefore have to be determined by goniometric measurement.

Cubic system	$a : b : c = 1 : 1 : 1.$	$\alpha = \beta = \gamma = 90^\circ.$
Hexagonal system	$a : b : c = 1 : 1 : 1.$	$\alpha = \beta = \gamma = ? .$
Tetragonal system	$a : b : c = 1 : 1 : ?$	$\alpha = \beta = \gamma = 90^\circ.$
Orthorhombic system	$a : b : c = ? : 1 : ?$	$\alpha = \beta = \gamma = 90^\circ.$
Monosymmetric system	$a : b : c = ? : 1 : ?$	$\alpha = \gamma = 90^\circ, \beta = ?$
Anorthic system	$a : b : c = ? : 1 : ?$	$\alpha = ?, \beta = ?, \gamma = ?$

The rhombohedral system is a subdivision of the hexagonal system, and the constants appertaining to both are similarly stated; both of these systems are frequently referred to axes of the form $a : a : a : c = 1 : 1 : 1 : ?$, the three equal axes a lying in a plane at mutual inclinations of 120° and perpendicular to the c -axis.

those of the trigonal axes of symmetry. Appropriate intercepts of the ordinary crystallographic axes will, however, serve for the purpose of dividing space into parallelepipedal cells equal in volume to the molecular or the valency volume, the three dimensions of the parallelepipedon giving the ratios of the minimum translations of the structure in the three axial directions. This, in most instances, suffices for purposes of comparing substances of similar crystalline structure, for, although the values compared do not necessarily express the minimum distances separating unit centres in the structure, they are similar functions of such distances.

The sets of equivalence parameters stated below will show that a method of calculation is now available which enables us to correlate the apparently very incongruent crystallographic data relating to series of compounds which may be regarded chemically as derived from the same parent substance.

The appended table gives the axial ratios and topic axial ratios (Gossner, *Zeit. Kryst. Min.*, 1904, 38, 154) for the orthorhombic hexa-halogen derivatives of ethane, together with the corresponding equivalence parameters. Gossner's axial ratios (*loc. cit.*, 504) for the monosymmetric pentabromoethane, namely, $a:b:c=0.8353:1:0.5655$, $\beta=111^\circ 5'$, are also included, but have been transposed by making $a(001)$, $m(012)$, and $q(111)$; this gives $a:b:c=0.5650:1:1.5590$, $\beta=91^\circ 19'$, numbers which are more in accordance with the distorted orthorhombic character of the crystals. The length of the c -axis of pentabromoethane has been divided by five for the purposes of the following calculation of the equivalence parameters:

	$a : b : c.$	$V.$	$\chi : \psi : \omega.$	$W.$	$x : y : z.$
$\text{CCl}_3 \cdot \text{CCl}_3$	0.5677 : 1 : 0.3160	113.34	4.8713 : 8.5808 : 2.7115	14	2.4260 : 4.2733 : 1.3503
$\text{CBr}_3 \cdot \text{Cl} \cdot \text{CCl}_3$	0.5612 : 1 : 0.3171	116.72	4.8760 : 8.6884 : 2.7551	14	2.4047 : 4.2849 : 1.3587
$\text{CBrCl}_3 \cdot \text{CBrCl}_3$	0.5646 : 1 : 0.3192	120.16	4.9647 : 8.7949 : 2.7520	14	2.4090 : 4.2669 : 1.3620
$\text{CBr}_3 \cdot \text{CBr}_3$	0.5639 : 1 : 0.3142	131.83	5.1099 : 9.0618 : 2.8472	14	2.4197 : 4.2911 : 1.3483
$\text{CHBr}_2 \cdot \text{CBr}_3$	0.5650 : 1 : 0.3118	126.46	$\beta=91^\circ 19'$	14	2.4294 : 4.2995 : 1.3406
Chlorobromonitro-phenol $\beta=114^\circ 38'$	1.0470 : 1 : 0.5994	118.7	6.2043 : 5.9257 : 3.5519	38	4.2443 : 4.0537 : 2.4298
Dibromonitro-phenol $\beta=114^\circ 37'$	1.0302 : 1 : 0.5912	121.1	6.2069 : 6.0249 : 3.5619	38	4.2179 : 4.0042 : 2.4205
Bromoiodonitro-phenol $\beta=114^\circ 14'$	1.0400 : 1 : 0.5802	129.03	6.4133 : 6.1667 : 3.5779	38	4.2669 : 4.1028 : 2.3804

The second part of the table deals with Gossner's data (*Zeit. Kryst. Min.*, 1905, 40, 84) for those derivatives of 1-chloro-3-bromo-5-nitro-6-hydroxybenzene in which the 1-chlorine atom is replaced by bromine and iodine.

Throughout the above two series the equivalence parameters are distinctly less variable than are the corresponding topic axial ratios, and in so far support our contention that the volumes of the spheres of atomic influence of hydrogen, chlorine, bromine, and iodine bear almost the same ratio to the corresponding molecular volumes. A

careful inspection of the above table will show, however, that the equivalence parameters have most advantage over the topic axial ratios, as a measure of the similarity of type of two allied substances, in those cases in which the molecular volumes differ most. It sometimes happens that the equivalence parameters preserve their constancy no better throughout a series of related compounds than do the topic axial ratios; this is only the case, however, when the molecular volumes are practically constant throughout the series. The values obtained by Jaeger (*Zeit. Kryst. Min.*, 1904, 38, 595) for the six isomeric tribromotoluenes afford an example of this kind.

When dealing with a series of related compounds, it often happens that the observed axial ratios of one or more members of the series do not give directly equivalence parameters in harmony with those of the rest of the series: in these cases, the selection of certain simple multiples of one or both of the axial ratios, a/b and c/b , as a basis from which to calculate the equivalence parameters, generally brings the substance into agreement in this respect with the other members of the series. The selection of these multiples is arbitrary, in that it is made without other directing indication than an approximate knowledge of what values the equivalence parameters should possess; its arbitrary character is connected with the fact that the numerical values of the axial ratios themselves are arbitrarily fixed, in that it is usually possible, on the basis of the goniometrical examination, to assign to a crystalline substance several sets of indices and axial ratios, all of which have the same experimental justification. And amongst these alternative sets of axial ratios one, in general, leads, without previous reduction, to the deduction of equivalence parameters in harmony with those of other members of the series.

An inspection of the possible simple multiples which can be selected shows that in most of the cases now dealt with only one leads to the required conformity of the equivalence parameters; this fact is the ground for the selection of that particular multiple. Thus, in the previous table, the fact that the only simple way of bringing the equivalence parameters of pentabromoethane into congruence with those of the hexa-halogen derivatives is by taking one-fifth of the length of the c -axis in calculating the values of x , y , and z , determines the choice of this multiple.

It may, however, be contended that by suitable manipulation of the most unfavourable set of axial ratios, any desired result may be obtained, and, without further discussing this point, we may admit that if, in any particular case, it is found necessary to select fractional multiples of the recorded axial ratios in order to exhibit relationships between the equivalence parameters, the demonstrative value of that

case is diminished. For the elucidation of every important point we have therefore selected, from the mass of crystallographic data available, cases in which complex fractionation of the axial ratios is unnecessary. All, however, who are experienced in crystallographic measurement recognise that two independent observers very commonly assign different parametral schemes to the same substance, and it cannot therefore be legitimately urged that in any large proportion of instances the stated axial ratios can without reduction be taken as referring to the molecular unit itself. And the fact that it is possible, throughout this paper, to offer a complete argumentative sequence based on unmanipulated axial ratios fully justifies the quotation for illustrative purposes of a number of cases of the other kind.

It should perhaps be pointed out that the detection or indication of morphotropic relationships between two substances exhibiting the axial ratios, $a' : b' : c'$ and $a'' : b'' : c''$, is generally effected by showing a correspondence between one or more of the ratios a/b , c/b , or a/c in both. As the only numerical data available are thus the values a'/b' , a''/b'' , c'/b' and c''/b'' , fallacy may well arise if too great advantage is taken of the fact that these ratios are simple fractional multiples of molecular dimensions in the several axial directions in the crystal structure. The extent to which the selection of simple multiples of the axial ratios may be legitimately applied is, however, much greater in the case of the equivalence parameters, because here the conditions are much more narrowly limited. Instead of having to select numbers which are consonant, as simple multiples, with the ratios a/b and c/b , we have here to satisfy the following much more rigid conditions. Given, for two instances, the axial ratios, $a' : b' : c'$ and $a'' : b'' : c''$, and the valency volumes, W' and W'' , select such simple multiples, pa' , qb' , rc' , ha'' , kb'' , and lc'' , of the axial ratios for the calculation of the equivalence parameters, x' , y' , z' , x'' , y'' , and z'' , as will satisfy the conditions that $x'y'z' = W'$, $x''y''z'' = W''$, $x'/pa' = y'/qb' = z'/rc'$, $x''/ha'' = y''/kb'' = z''/lc''$, and will make one, two, or all of the values x' , y' , and z' equal to one, two, or all of the values x'' , y'' , and z'' .

As a somewhat extreme instance of the method of treatment adopted we submit the following table, from which we conclude that the quantitative data referring to camphor and its orthorhombic halogen derivatives are wholly in accordance with the hypothesis as to molecular constitution now put forward; in this series, the valency volume $W = 60$. The axial ratios for the hexagonal form of camphor, namely, $a : c = 1 : 1.6202$, are thrown into the orthorhombic form of $a : b : c = 0.8660 : 1 : 1.6202$. In this table, as in others given later, the values of x , y , and z are tabulated in such an order as reveals the relation between the several sets.

Substance.	$a : b : c.$	Multiples of axial ratios		
		selected.	$x : y : z.$	
Camphor *	0.8660 : 1 : 1.6202		2.9943 : 3.1577 : 5.6021	
α -Dibromocamphor † ...	0.7925 : 1 : 0.5143	$2a, 5c/3$	2.9959 : 3.4949 : 5.5395	
β -Dibromocamphor † ...	0.9527 : 1 : 0.5186	$3b/5$	3.0107 : 3.4832 : 5.5308	
α - π -Dibromocamphor ‡	0.6860 : 1 : 0.3323	$5a/4, 5c$	2.9498 : 3.4100 : 5.7156	
β -Monobromocamphor §	1.0620 : 1 : 0.8220	$a/2$	2.9084 : 3.5382 : 5.6363	

The above sets of figures show that the axial ratios of members of a series of related substances having the same valency volume may be interpreted by means of the equivalence parameters so as to indicate similarity of chemical structure. Camphor and its various halogen derivatives may be supposed to have practically identical molecular configurations, and, in accordance with the views expressed above, should possess nearly identical relative molecular dimensions if really built up from spheres of atomic influence of the volumes four, two, and one; the possibility of assigning almost the same set of equivalence parameters to all the members of the series is in entire harmony with this conclusion. But before proceeding to a closer study of the assemblages representing chemical substances, it is desirable to demonstrate that the new kind of axial ratios render valuable service in expressing and elucidating morphotropic and constitutional relations between substances of different valency volumes.

The following table gives data for the orthorhombic d - ω - and dl - ω -bromocamphoric anhydrides (*Acta Soc. Scient. Fenn.*, 1896, **21**, 204) (the value of a being reduced to $2/3$), for the monosymmetric d - π -bromocamphoric anhydride (*Trans.*, 1897, **71**, 970) (the a value being reduced to $4/3$), the orthorhombic d -camphoric anhydride and the orthorhombic addition compound of d -camphoric acid with acetone (*Trans.*, 1896, **69**, 1696) (the axial lengths being unaltered).

Substance.	$H.$	$a : b : c.$	$x : y : z.$
d - ω - $C_{10}H_{13}BrO_3$	60	0.5920 : 1 : 0.5775	3.3145 : 3.2332 : 5.5988
dl - ω - $C_{10}H_{13}BrO_3$	60	0.5816 : 1 : 0.5799	3.2710 : 3.2615 : 5.6241
d - π - $C_{10}H_{13}BrO_3$	60	1.0835 : 1 : 1.6453	3.4985 : 3.2286 : 5.3125
$\beta = 88^\circ 59' 30''$			
d - $C_{10}H_{14}O_3$	60	1.0011 : 1 : 1.7270	3.2654 : 3.2618 : 5.6331
d - $C_{10}H_{16}O_4, \frac{1}{2}(CH_3)_2CO$	74	1.2386 : 1 : 1.7172	4.0435 : 3.2646 : 5.6060

A very close approximation to agreement between the equivalence parameters is observed throughout the table; the largest discrepancies are to be noted in the x and z values for the d - π -bromocamphoric anhydride, and the reason lies in the fact that the directions x and z are affected by the shear which gives the crystals their monosymmetric symmetry. But on comparing the values for the addition compound of camphoric acid and acetone with those of the previous substances, it is seen that

* des Cloizeaux, *Compt. rend.*, 1859, **48**, 1064.

† Zepharovich, *Zeit. Kryst. Min.*, 1883, **7**, 588.

‡ Kipping and Pope, *Trans.*, 1895, **67**, 371.

§ Armstrong and Lowry, *Trans.*, 1902, **81**, 1466.

whilst the values y and z agree closely right through the table, the x value for the addition compound is much in excess of the other x values. This suggests that on introducing water and acetone into the close-packed assemblage representing camphoric anhydride, the new assemblage retains the y and z dimensions of the original one, and that the anhydride assemblage merely opens out in the direction of x to admit of the new components entering as a close-packed layer or pad between the two surfaces exposed.

The kind of relation thus shown to exist between the camphoric anhydride and the camphoric acid addition compound assemblages is of frequent occurrence, notably in the case of double salts and substances crystallising with the solvent. The interpretation of the relationship in the light of our fundamental conception with the aid of the equivalence parameters at once elucidates a number of mineralogical observations which, in spite of their important character, have hitherto remained without explanation. Thus, it has long been known that the monosymmetric mineral chondrodite, $\text{Mg}_3(\text{SiO}_4)_2 \cdot 2\text{Mg}(\text{F})(\text{OH})$, the orthorhombic humite, $\text{Mg}_5(\text{SiO}_4)_3 \cdot 2\text{Mg}(\text{F})(\text{OH})$, and the monosymmetric clinohumite, $\text{Mg}_7(\text{SiO}_4)_4 \cdot 2\text{Mg}(\text{F})(\text{OH})$, in each of which the angle $\beta = 90^\circ$, are morphotropically related in such a way that, whilst the ratio $a : b$ is practically the same in all, the ratio $c : b$ is in the proportion of 5 : 7 : 9 for the three substances respectively (Penfield and Howe, *Zeit. Kryst. Min.*, 1894, 23, 78). On summing up the valency volumes of these substances, regarding the isomorphous constituents F and OH as present in equivalent proportion, the values 38, 54, and 70 are obtained; these numbers are practically in the ratio of 5 : 7 : 9. On calculating the equivalence parameters as in the appended table, it is seen that the values of x and y remain almost the same throughout the series, whilst z increases in the proportion stated; the values of z/W are given in the last column.

Mineral.	W .	$a : b : c$.	$x : y : z$.	z/W .
Chondrodite.....	38	1·08639 : 1 : 3·14472	2·4249 : 2·2323 : 7·0199	0·18473
Humite.....	54	1·08021 : 1 : 4·40334	2·4278 : 2·2475 : 9·8965	0·18327
Clinohumite.....	70	1·08028 : 1 : 5·65883	2·4349 : 2·2540 : 12·7547	0·18221

The practical constancy of the values x , y , and z/W indicates that the increment of the series, Mg_2SiO_4 , is introduced as a layer parallel to the directions a and b and perpendicular to the direction c , so that the dimension of the latter is the only one of the three which is materially affected; it is further clear that the effect produced upon the c -axis by insertion of the group is proportional to its valency volume.

The increment of composition in the series is Mg_2SiO_4 , the composition of forsterite; by subtracting this increment from the composition of chondrodite, the residue $\text{MgSiO}_4 \cdot 2\text{Mg}(\text{F})(\text{OH})$, is obtained; this is the composition attributed to prolectite (Sjögren, *Zeit. Kryst. Min.*, 1896,

26, 103). The equivalence parameters and the axial ratios for the two latter minerals should thus be deducible from the data given for the above three; the values calculated on this assumption and those actually observed are given in the following table. The determined length of the axis b has been halved in the numbers given for forsterite.

Proectite, $W=22$:

	a : b : c .	x : y : z .
Observed	1·0803 : 1 : 1·8862	2·3877 : 2·2102 : 4·1689
Calculated	1·0822 : 1 : 1·8500	2·4292 : 2·2116 : 4·1526

Forsterite, $W=16$:

	a : b : c .	x : y : z .
Observed	0·9296 : 1 : 1·1714	2·1492 : 2·2769 : 2·8691
Calculated	0·9240 : 1 : 1·1801	2·4292 : 2·2446 : 2·8674

It will be admitted that the agreement between the observed and calculated numbers is very close in view of the comparatively rough manner in which these two minerals have been characterised.

The above results may be summarised by saying that in the crystalline state the spaces occupied by the groups or radicles common to the several members of the series assume similar forms, and the amount of space occupied by any such radicle or group bears to the amount of space occupied by the whole molecule the ratio borne by the valency volume of the component group to the valency volume of the molecule. Results of a similar nature are repeatedly stated in the course of this paper, and it is claimed that these are observations of fact which must be accepted quite independently of any judgment which may be passed upon the theoretical views advanced to explain them.

The extent to which the present mode of treatment is independent of crystalline system is worthy of note; the monosymmetric chondrodite becomes orthorhombic by the addition of Mg_2SiO_4 , whilst the addition of the second increment of Mg_2SiO_4 reduces the symmetry to that of the monosymmetric clinohumite. This fact has interesting applications to the isomorphism and morphotropic relationships existing between naturally occurring silicates belonging to different crystalline systems.

That the same sort of relationship holds between salts containing various proportions of water of crystallisation is indicated by the following comparison of the tetragonal and orthorhombic nickel sulphates containing $6H_2O$ and $7H_2O$ respectively, and the two orthorhombic sodium carbonates containing $1H_2O$ and $7H_2O$ (from Rammelsberg, *Kryst-physik. Chem.*, I, 417 and 548).

Salt.	W .	a : b : c .	x : y : z .	Multiples of axial ratios selected.
$NiSO_4 \cdot 6H_2O$	36	1·0000 : 1 : 1·9060	2·6631 : 2·6631 : 5·0760	
$NiSO_4 \cdot 7H_2O$	40	0·5656 : 1 : 0·9815	2·5729 : 2·6214 : 6·9307	$4a$
$Na_2CO_3 \cdot H_2O$	16	0·8268 : 1 : 0·8088	2·3824 : 2·3306 : 2·8815	
$Na_2CO_3 \cdot 7H_2O$	40	0·7510 : 1 : 0·3600	2·3990 : 2·5022 : 6·6637	$a/2$

It will be seen that on calculating the equivalence parameters, using the simple multiples of the axial ratios noted in the last column, two of the equivalence parameters remain nearly unchanged during the hydration of the salt; the whole effect of the introduction of the water of crystallisation can thus be thrown upon one of the three axial directions. That is to say, the water entering the structure may be regarded as forming a layer in the crystalline structure, and as being so symmetrically introduced as to affect but one axial direction. This same reasoning is applicable to a number of compounds containing water of crystallisation, but in some cases requires modification: for example, the introduction of water of crystallisation to form a cubic crystalline substance must take place symmetrically in the various equivalent directions throughout the assemblage.

It is instructive to notice that in passing from the tetragonal salt, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, to the orthorhombic hydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, but very slight disturbance of the symmetry occurs; the orthorhombic salt, both in crystal habit and axial ratios, approximates closely to tetragonal symmetry.

The effect both of polymorphism and of the introduction of water of crystallisation is seen in the following table relating to the optically active *trans*- π -camphanic acids, $\text{C}_{10}\text{H}_{14}\text{O}_4$, which crystallises with $1\text{H}_2\text{O}$ in a monosymmetric and also in an orthorhombic form, and without water in an orthorhombic form (Kipping and Pope, *Trans.*, 1897, 71, 962).

	Multiples of axial ratios			
	<i>a</i> : <i>b</i> : <i>c</i> .	taken.	<i>x</i> : <i>y</i> : <i>z</i> .	<i>W</i> .
C ₁₀ H ₁₄ O ₄ .H ₂ O ...	1·9110 : 1 : 1·4627	2 <i>b</i>	4·4514 : 4·6588 : 3·4072	66
	<i>β</i> = 69° 5'			
C ₁₀ H ₁₄ O ₄ .H ₂ O ...	0·9158 : 1 : 0·3551	2 <i>c</i>	4·2716 : 4·6643 : 3·3126	66
C ₁₀ H ₁₄ O ₄	0·9584 : 1 : 0·7292		4·2745 : 4·4600 : 3·2522	62

The difference in crystalline form of the two hydrated modifications of the acid causes change in the dimensions in the directions *a* and *c*, those namely which are involved in the shearing process by which the monosymmetric system is derived from the orthorhombic; the direction *b* remains practically unaltered, so that the *y*-value is nearly the same for the first two substances. The removal of the molecule of water of crystallisation from the orthorhombic form causes practically no change in the *x*-value, and produces most alteration in the direction of the *b*-axis.

The mode suggested above of regarding molecular complexes such as double salts, compounds containing solvent of crystallisation, and the like, naturally directs attention to one aspect of molecular composition which has hitherto not been considered as of importance. Some simple numerical relation is found to subsist between the valency volumes of the two or more molecular components making up the system. This

simple relationship is most prominent in the double salts; the following examples, typical of large classes of substances, to which the valency volumes of the component complexes are appended, will indicate the kind of relation observed.

$K_2SO_4, Al_2(SO_4)_3, 24H_2O$	Valency volume =	$12 + 36 + 96$
$(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$	„ „	= $24 + 36 + 96$
$2KCl, CuCl_2, 6H_2O$	„ „	= $4 + 4 + 24$
$K_2SO_4, CuSO_4, 6H_2O$	„ „	= $12 + 12 + 24$

In each of the above and in other cases representing double salts the valency volumes of the component complexes are in a simple ratio one to the other and to the total valency volume. In connexion with these observations it may be remarked that the close-packing together of two molecular surfaces evidently requires that the spacing of the spheres of influence shall be congruent—in other words, that the distances separating corresponding parts on the one surface shall be simple fractions of such distances on the other; and if this holds good in the three principal plane directions, it involves a simple numerical relation between the volumes of the associated complexes. The applicability of this principle to cases where the water of crystallisation is intercalated in isolated groups of one or more molecular complexes so as to produce crystalline assemblages of the high symmetry associated with the cubic or hexagonal systems, as in the alums, and not inserted in layers, as in assemblages of lower crystallographic symmetry, is more directly apparent.

The Partitioning of Close-packed Assemblages.

All symmetrical and homogeneous close-packed assemblages can be partitioned in a symmetrical and homogeneous way into similar cells or units. And, after an appropriate partitioning, the unit or cell into which the close-packed assemblage is resolved represents in composition, constitution, and configuration the chemical molecule itself; each cell of the partitioning is thus occupied by one chemical molecule, and the partitioning is of such a nature that the cell walls do not intersect any component sphere. Thus, one close-packed assemblage of the general composition, C_nH_{2n-6} , can be partitioned symmetrically into units of the composition, C_6H_6 , and represents benzene; another representing toluene can be partitioned into units of the composition C_7H_8 ; and three others, representing the three xylenes, are partitionable into units of the composition C_8H_{10} . In many cases the partitioning which has to be resorted to for the purpose of resolving the close-packed assemblage into the similar groups representing molecules is, owing to geometrical reasons, of lower symmetry than the original assemblage; the partitioning is therefore arbitrary, in that

it leaves unsevered some contacts between neighbouring spheres in the assemblage which are of precisely the same quality as others which it ruptures; and some of the spheres left mutually attached after the partitioning have, previous thereto, no closer association than others which the partitioning allots to different molecules. Many close-packed assemblages can be partitioned in two distinct ways, but so that the units resulting from both partitionings are constitutionally identical; in other cases two distinct methods of partitioning are possible, and give rise to units or molecules exhibiting isomerism. Many of the peculiarities observed in the substitution of aromatic hydrocarbons are immediately traceable to this property of the corresponding close-packed assemblages. Further, many other close-packed assemblages can be partitioned in two ways in such a manner that the units or molecules which result are constitutionally dissimilar; these assemblages represent tautomeric or isodynamic substances, and, as will be shown in a later paper, the two kinds of unit produced represent in every way the two forms of the substances concerned.

For a close-packed assemblage to represent a particular substance, it must not only be a homogeneous one in which the spheres of influence of the component atoms are present in the proportions indicated by the molecular composition, but it should exhibit the crystalline symmetry of the substance; moreover, groups of associated spheres of atomic influence should be recognisable in it, identical in composition and configuration with the chemical molecule itself. And since the assemblage is a homogeneous arrangement of spheres of atomic influence grouped to form similar molecules, it must be homogeneously partitionable into space-units, all identical and each representing a chemical molecule in composition and configuration. It is evident that isomerism introduces a complication; as will be shown later, in cases where isomerism is possible and not traceable to varieties of partitioning of the same assemblage, several close-packed assemblages are obtainable corresponding in number and character to the various known isomerides; these alternative assemblages are all close-packed, but not necessarily all equally densely packed. We have therefore to derive these isomeric assemblages from others by a process of substitution or distortion, and to show what provision can be made to ensure their separate and individual existence: that is, to indicate a method by which one assemblage can be geometrically prevented from lapsing into an alternative or isomeric assemblage merely because the latter happens to be slightly more densely packed. The necessary condition in all cases is that the disposition in the homogeneous assemblage of the spheres of atomic influence with respect to one another is such that if represented by stacks of spheres of appropriate sizes, the arrangements presented are equilibrium arrangements in

close-packing. An assemblage of spheres is described as close-packed if it cannot be caused to pack more closely by any process of shearing or distortion unaccompanied by "remarshalling" of its parts; the meaning attached to the term remarshalling is defined by the statement that an assemblage retains its original marshalling, after subjection to shearing or distortion, when no sphere of the assemblage has been shifted during the distortion past the narrowest part of one of the small apertures found between the other spheres immediately surrounding it. This mode of considering close-packing permits of the existence in close-packed assemblages of groups of spheres or of radicles whose individual shape is such that the space occupied by the whole assemblage is greater than would be requisite if the constituent spheres were separately stacked or were differently arranged; in other words, there are in many cases several equilibrium arrangements in close-packing of the same set of spheres; these arrangements present slightly different densities of packing. In the numerous cases discussed later it will be seen that the alternative arrangements provided correspond closely with the number and nature of the isomerides actually obtainable.

The geometrical idea of marshalling acquires further importance when it is considered that most of the available data of a quantitative character are crystallographic, and that by hypothesis the crystal structure is a close-packed assemblage of the molecules. During the process of crystallisation the molecules, by the operation of the two forces previously referred to, would become closely and homogeneously fitted together, and be subject to such distortion or deformation as may be necessary for this purpose. The nature of this distortion can, in many cases, be exactly traced, and is not of such a kind as leads to remarshalling.

The Representation of Molecular Complexes.

The purely mechanical view of molecular structure above foreshadowed is most conveniently depicted by a purely mechanical method. The statical equilibrium established in close-packed molecular assemblages as a result of the simultaneous attraction and repulsion of the atoms is expressed graphically in a very complete manner by representing each sphere of atomic influence by an elastic ball of appropriate diameter composed of soft, solid indiarubber, which, while deformable, is practically incompressible, a very considerable number of balls being employed, and the mass subjected to uniform pressure nearly sufficient to close up the interstices by flattening the spheres at the places of contact. For practical purposes hard balls are more convenient to handle; if slightly flattened at the points of con-

tact, they represent sufficiently well the arrangement under consideration.

If balls of appropriate magnitudes and appropriate degrees of compressibility are selected, they can be grouped together and close-packed under a general pressure so as to simulate accurately both chemical molecules and assemblages of chemical molecules.

The Configuration of Aromatic Compounds.

It will be convenient at once to apply the geometrical principles developed above to some particular series of chemical compounds, and for this purpose we select a number of typical aromatic substances, because these have been so completely examined crystallographically as to allow of a direct control upon the validity of the methods which we employ.

The problem involved in determining the configuration of the benzene complex, stated in the terms introduced in the foregoing pages, is that of finding an arrangement of spheres of two sizes, six of each, of such a form as corresponds to the general properties of benzene, and of such a configuration that an indefinitely large number of identical groups of the kind can, without remarrying, be close-packed so as to give an assemblage exhibiting the crystalline symmetry of benzene. The problem is very precisely defined, in that the known molecular composition and the known relations between the six hydrogen atoms in the molecule which are expressed in the isomerism of the di- and tri-substitution derivatives, and also the known crystalline form, all limit its solution; to these conditions must be added that the assemblage for benzene must be capable of conversion, by simple substitutions in which the type of the units is not changed, into assemblages which conform in chemical and crystallographic respects to the properties of benzene derivatives and of other aromatic hydrocarbons. A further important limitation is imposed by the new condition that the relative volumes of the spheres of atomic influence composing the various assemblages must be directly proportional to their fundamental valencies.

The solution of the problem is the following: Six spheres, each of volume four, are placed in contact so that their centres lie at the apices of a regular octahedron; six spheres, each of about volume one, are then placed in six of the eight similar hollows lying round the octahedral group in such a manner that the two unoccupied hollows are diametrically opposite each other. The resulting arrangement is shown in plan in Fig. 1; it is in certain respects similar to some of the benzene configurations deduced from Werner's theory (Bloch, *Theorie des Kohlenstoffatoms*, 1903, 72), and, like the latter,

leads to the derivation of three isomeric di-derivatives. It indicates also the derivability of one, two, and three tri-derivatives from the para- meta- and ortho-derivatives of benzene respectively. The configuration depicted is, in fact, in accordance with the general properties of benzene, in so far as these are expressed by the isomerism of aromatic compounds.

We have next to show how complexes in which the parts are marshalled as indicated can be close-packed so as to form a homogeneous assemblage exhibiting the symmetry and axial ratios of crystalline benzene; this is accomplished by the following series of numbered steps:

FIG. 1.

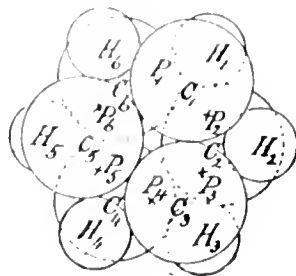
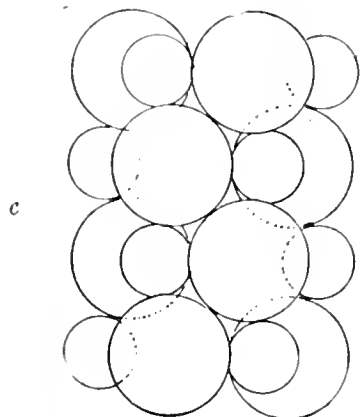
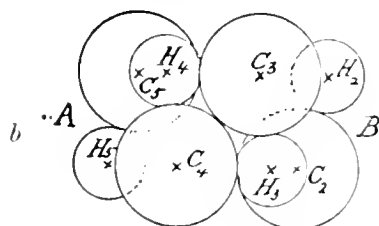
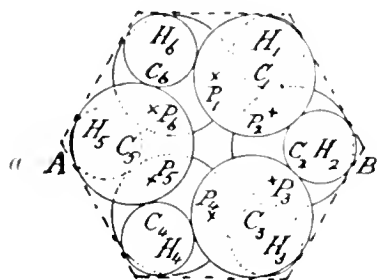


FIG. 2.



(1.) The complexes are piled vertically in close-packed columns, the faces in contact being those which do not carry small or hydrogen spheres; in the column the individual complexes have the same orientation, and each small sphere is in contact with three larger ones.

(2.) The column thus obtained is slightly shortened by compression, so that the centres of the larger spheres separate until the smaller spheres touch four instead of three of them; the arrangement which results, employing complexes of hard spheres, is shown in plan and elevation in Fig. 2, *a*, *b*, and *c*. The two sizes of spheres alternate regularly in the vertical column, as indicated in Fig. 2*c*, and a geometrical partitioning divides it into cells each containing two consecutive layers of the column, as shown in Fig. 2*b*. The shortening of the column does not so distort it as to lead to remarshalling.

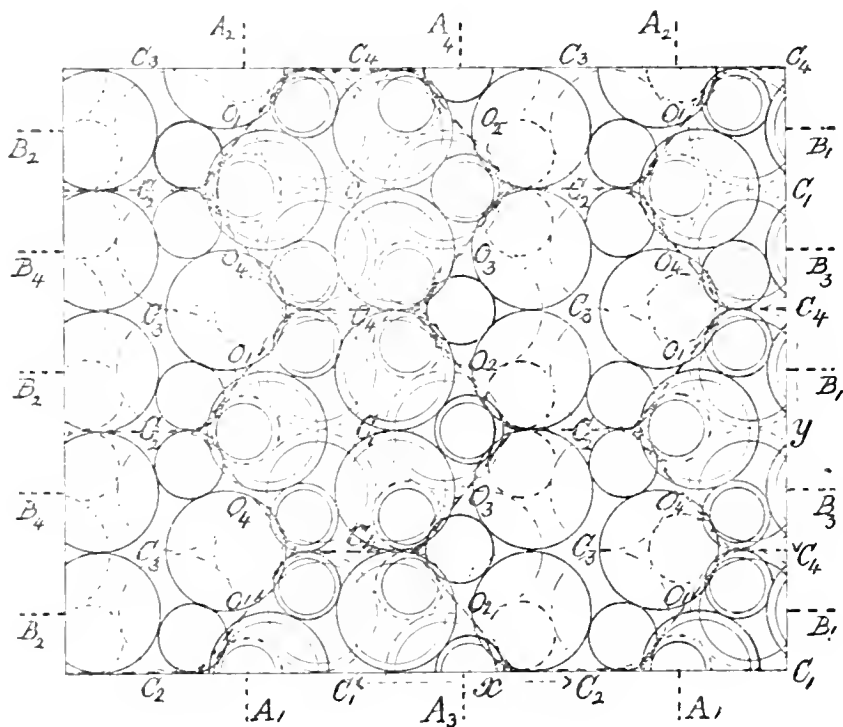
(3.) Columns thus built up are placed in contact side by side and similarly orientated so as to form walls having the direction C_1C_4 or C_2C_3 indicated in Fig. 3.

(4.) These walls are then packed side by side so as to fill space as shown in Fig. 3, and for the purpose of achieving the closest possible

packing of a number of walls, a, b, c, d, e, f , &c., the walls a, c, e must be placed at a somewhat different level from the alternate walls, b, d, f ; the successive walls in the structure then interlock. The raising of alternate walls with respect to the others is indicated in Fig. 3, and other subsequent figures, by drawing the circles representing the one level in single lines, and those representing another level in double lines.

(5.) The closeness of the packing is further increased by again slightly distorting each complex, without remarshalling; the nature of this distortion will be realised on comparing Fig. 1, representing

FIG. 3.



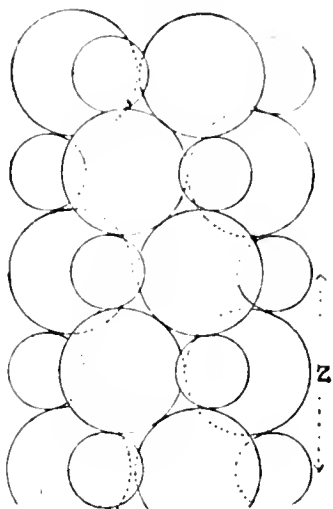
the undistorted complex, with Fig. 2a, showing the effect of the first distortion involved in the shortening of the columns, and also comparing it with one complex of hexagonal contour in Fig. 3. Fig. 4 indicates the effect of the second distortion on the elevation of the columns. The assemblage which has thus been obtained is that representative of crystalline benzene.

The several distortions just above described are geometrically very simple, and assist in the achievement of the closest possible packing of the benzene complexes, with the aid of any distortion or shear which does not involve a remarshalling of the parts of the complexes. We suggest that no adjustment other than those described assists the close-packing, and that the arrangement finally depicted in Fig. 3 is the most close-

packed possible. It remains now to show that this assemblage is strictly in accordance with the crystalline form of the hydrocarbon, and must therefore be regarded as representing the distribution in space of the atoms and molecules which make up benzene in the crystalline state.

Benzene crystallises in the holohedral orthorhombic system, and exhibits the axial ratios $a : b : c = 0.891 : 1 : 0.799$ (Groth); these values give, since the valency volume W is 30, the equivalence parameters $x : y : z = 3.101 : 3.480 : 2.780$. The structure depicted in Fig. 3 is also holohedrally orthorhombic in symmetry, but, in order that it may correctly simulate the crystal structure of benzene, it must be possible to select three translation dimensions within it, which lie in directions parallel to the three axes of the orthorhombic symmetry, and for these translations, or simple multiples of them, to have the values of the equivalence parameters x , y , and z . The appropriate translation dimensions are shown in Figs. 3 and 4; and these drawings have been made to the scale of $x : y : z = 3.101 : 3.480 : 2.780$. The length x is one-half a translation along the axis a , y is twice the diameter of a large or carbon sphere, and z is, as indicated in Fig. 4, very slightly less than the sum of the diameters of a large and a small sphere; the product, $xyz = W$, is the minimum unit volume of the assemblage. The dimensions of the structure represented in Figs. 3 and 4, as well as the symmetry, are therefore in accordance with those of crystallised benzene.

FIG. 4.



The type of homogeneous structure thus assigned to the benzene assemblage is that marked No. 54 of Barlow's list (*Zeit. Kryst. Min.*, 1894, 23, 1), and is No. 14 of Sohncke's sixty-five systems with a centre of symmetry added. The positions of the different kinds of digonal screw axes (c) which lie perpendicular to the plane of Fig. 3 are marked C_1, C_2, C_3, C_4 . The digonal screw axes (both a and b) which lie parallel to the plane of Fig. 3 pass midway between these axes; their projections are marked $A_1A_2, A_3A_4, B_1B_2, B_3B_4$. The centres of symmetry lie on the axes whose projections, A_1A_2, A_3A_4 , are shown on Fig. 3, and are found at the points where these axes intersect planes drawn perpendicular to the plane of the figure through the axes B_1B_2, B_3B_4 ; their projections are marked O_1, O_2, O_3, O_4 . The axes C_1, C_2 , &c., all lie in planes of symmetry which are perpendicular to the plane of Fig. 3, and both the other sets of planes of symmetry are planes of gliding-symmetry. The difference in level of the nearest identical

layers of two interlocked walls of columns is seen from Fig. 4 to be $z/4$, z being the prism-translation which represents the vertical or c -axis of the crystal.

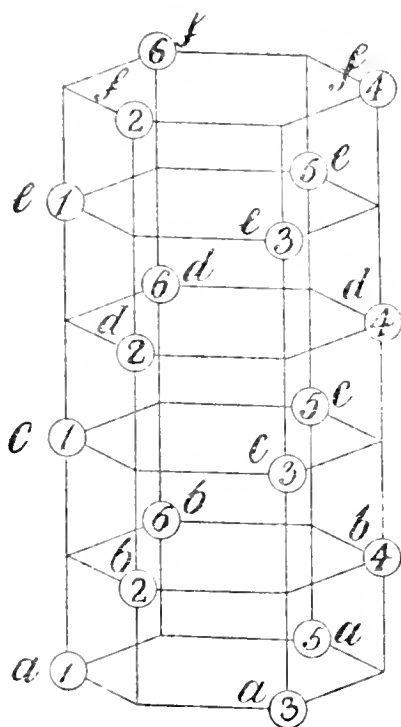
Although the highly symmetrical configuration of the benzene molecule depicted in Fig. 1 undergoes some distortion, unaccompanied by remarshalling, when packed into the structure shown in Fig. 3, it must be concluded that the distorted configuration occurs only in the crystalline state. There is no need to suppose that this temporary distortion survives the disintegration of the assemblage consequent on destruction of the crystalline structure, so that, for purposes of chemical reaction, and when separated from close-packed association

with its companion units, the symmetry of the molecule should be regarded as the highest which the complex representing it is able to assume without remarshalling of its component spheres. This is of universal application, and in this, and all other cases, the nature of the marshalling must be regarded as the characterising feature of the chemical molecule.

The objection may be taken to the benzene configuration now suggested which was raised against, and which proved fatal to, the solid configurations proposed by Ladenburg (see Lewkowitsch, *Trans.*, 1888, 53, 781; *Ber.*, 1883, 16, 1576), namely, that all solid configurations of the benzene molecule lead to enantiomorphism amongst the di- and tri-substitution derivatives, an enantiomorphism which has not hitherto

been discovered. This objection is, however, groundless as applied to the present work, and for the following reason. In the column represented as an element of the structure in Fig. 4, the hydrogen spheres lie three in each of a set of parallel planes represented by a, b, c, d, e, f , of Fig. 5 and at the numbered points. And in accordance with what has been explained above, the geometrical partitioning of the column involves the separation of any two of its consecutive layers to form a free molecule of the hydrocarbon; alternative partitionings are thus possible, giving as separate complexes the pairs of layers ab, cd, ef , or bc, de, fg . And if the hydrogen spheres, 1, 2, 3, 4, 5, and 6, are replaced in any symmetrical manner in the layers a, b, c , &c., of the column, so as to lead to enantiomorphism on partition-

FIG. 5.



ing into the units *ab*, *cd*, *ef*, the simultaneous occurrence in another column of partitioning into the units *bc*, *de*, *fg*, will lead to the production of units or molecules enantiomorphously related to the former, and the whole disintegrated structure will be externally compensated. Therefore, although many of the di- and tri-derivatives of benzene must possess enantiomorphous configurations, they could not exist in the non-crystalline state in an optically active form, because the alternative partitioning annuls the optical activity.

The benzene assemblage is thus one in which two distinct geometrical partitionings can be performed, each leading to a subdivision into identical benzene molecules. Such alternative partitioning is in many cases possible; as already indicated (p. 1690), in certain cases this leads to the production of alternative constitutions. In a later paper we shall show, for example, that the assemblage representative of phloroglucinol is partitionable in two ways, the one leading to the configuration of the symmetrical trihydroxybenzene, the other to that of the 1:3:5-triketohexamethylene. The possibility of such an alternative geometrical partitioning of the appropriate homogeneous assemblage affords an explanation of the existence of enolic and ketonic isomerides.

Without at present pursuing this particular aspect of alternative geometrical partitioning further, one application of it can at once be made which illustrates the kind of way in which the new method of formulating molecular structures elucidates certain obscure points in the behaviour of benzene derivatives. The numbering in Fig. 5 is that conventionally used for distinguishing the six hydrogen atoms in the Kekulé formula of benzene, and the possibilities of isomerism attending the formation of di-derivatives of the hydrocarbon can be conveniently traced on Fig. 5 with the aid of the numbering and lettering given. The production of a mono-substitution derivative C_6H_5X necessitates the replacement of one hydrogen sphere in each alternate layer *a*, *c*, *e*, *g*, or *b*, *d*, *f*, *h*, by the group *X*; the introduction of a second group *X* to give the derivative $C_6H_4X_2$ may be brought about in two generically distinct ways: the second group *X* may enter the column in the same layers in which the first group *X* was introduced, leaving the alternate layers still unsubstituted, and in this case a meta-di-derivative alone will be formed; or the second group *X* may be introduced into the alternate layers, into which the *X* groups did not originally enter, and then an ortho- or para-derivative, or both, will be formed. A complete geometrical difference in kind thus exists between the derivation of the 1:3-di-derivative and that of the 1:2- and 1:4-isomerides; this is wholly in harmony with the observed chemical facts.

Further, suppose that the two substituting groups *X* are in-

troduced symmetrically into the column shown in Fig. 5 ; several geometrically distinct possibilities occur, but attention need here only be directed to one, namely, to the result obtained by substituting the hydrogen spheres $a_1, b_4, c_3, d_6, e_5, f_2, g_1, h_4$, &c., each by the group X . This type of substitution is highly symmetrical, and on subsequently partitioning the column, the units or molecules, $a_1b_4, c_3d_6, e_5f_2, g_1h_4$, all of the para constitution, result from the one kind of partitioning, whilst the other kind of partitioning leads to the production of the ortho-isomeride, $b_4c_3, d_6e_5, f_2g_1, h_4i_3$. The application, in different parts of the same assemblage, of the two partitionings leads to the simultaneous production of an ortho- and a para-di-derivative.

From the foregoing it will be seen that our method of regarding chemical structure is at once applicable to the facts summarised in the para-, ortho-, and meta-law ; it offers, in fact, a mechanism illustrating the facts that, if a meta-di-derivative of benzene is formed in any particular reaction, it is, in general, practically the sole product, whilst if an ortho-derivative is formed, it is, in general, accompanied by a large proportion of the para-isomeride (compare Armstrong, *Trans.*, 1887, **51**, 258).

In deducing the above configuration for benzene we have dealt only with close-packed arrangements of spheres in contact ; these spheres are conceived merely as the regions of space inhabited by distinct atoms, and this method of treatment, as already indicated, does not represent the truth with precise accuracy. The real state of the assemblage is, as has been said, better represented by the packing of elastic spheres subjected to a general pressure so as practically to eliminate the interstitial space ; it is only for convenience of representation that interstitial spaces are shown in the diagrams. As the assemblages represented, in which interstitial space is shown, would be converted into the correct assemblages containing no interstitial space, if the spheres were supposed elastic and subjected to appropriate pressure, the validity of the argument is not affected, because the relative dimensions of the assemblages are practically unaffected by the pressure.

The same type of assemblage as has been assigned to benzene is in accordance with the crystallographic data for hexachloro- and hexabromo-benzene ; these are pseudotrigonal and have been described by Fels (*Zeit. Kryst. Min.*, 1900, **32**, 367) as monosymmetric with the following axial ratios :

$$\text{C}_6\text{Cl}_6, a : b : c = 2.0993 : 1 : 4.3220, \beta = 116^\circ 52'.$$

$$\text{C}_6\text{Br}_6 \quad ,, \quad = 2.0903 : 1 : 4.2620, \quad ,, = 116^\circ 28' 30''.$$

These axial ratios are simplified by changing the forms $\{100\}$,

$\{001\}$, $\{102\}$, and $\{111\}$, to $\{101\}$, $\{100\}$, $\{101\}$, and $\{011\}$; this gives:

$$\text{C}_6\text{Cl}_6, a:b:c=2.1012:1:3.8618, \beta=87^\circ 49' 45''.$$

$$\text{C}_6\text{Br}_6, \quad,, \quad=2.0902:1:3.8183, \quad,,=87^\circ 18'.$$

On taking, in these values, $2a$ and $5b$, the equivalence parameters become compatible with those of benzene, namely:

$$\text{C}_6\text{H}_6, x:y:z=3.101:3.480:2.780, \beta=90^\circ.$$

$$\text{C}_6\text{Cl}_6, \quad,, \quad=3.0169:3.5894:2.7724, \quad,,=87^\circ 49' 45''.$$

$$\text{C}_6\text{Br}_6, \quad,, \quad=3.0181:3.6097:2.7587, \quad,,=87^\circ 18'.$$

So far as is known, benzene is not dimorphous, but it is interesting to notice that an alternative close-packed arrangement exists of units possessing the marshalling shown in Figs. 1 and 2; this alternative crystallographic arrangement of the units apparently occurs in the known crystalline modifications of some of the halogen derivatives of benzene.

The alternative arrangement referred to is of highly symmetrical marshalling, and may be regarded as consisting of layers of spheres one of which is depicted in Fig. 6, arranged one upon the other in rhombohedral symmetry; any two successive layers are thus arranged as shown in Fig. 7*a*, and form one stratum of benzene complexes, the centres of the latter lying at the points *A*. Fig. 7*b* shows how the next stratum of two layers has to be superposed upon that of Fig. 7*a*: Fig. 7*c*, how the next stratum lies upon that of Fig. 7*b*; this mode of superposition, which is designed so as to produce close-packing, leads to rhombohedral symmetry. The spheres of the fourth stratum, neglecting any slight distortion, come vertically over the corresponding ones of the first, and thus the first and fourth strata have the same projection. The centres of the small or hydrogen spheres do not lie exactly in the same planes as the large or carbon spheres of the same layer. The contour of the set of spheres constituting one benzene unit or molecule grouped about the centre *A* in Fig. 7*a* will be easily distinguished and seen to be identical in marshalling with that of Figs. 1 and 2.

Benzene units or molecules of the marshalling depicted in Figs. 1 and 2 can thus be packed closely in two alternative modes, the one indicated in Fig. 3, the other in Figs. 7*a*, *b*, and *c*. The alternative assemblages thus indicated may be geometrically distinguished in the following way.

It is well known that an indefinitely large number of equal spheres can be close-packed in either cubic or holohedral hexagonal symmetry; in the latter case, alternate triangularly arranged layers lie vertically over one another, and the two sets of alternate layers of which the

FIG. 6.

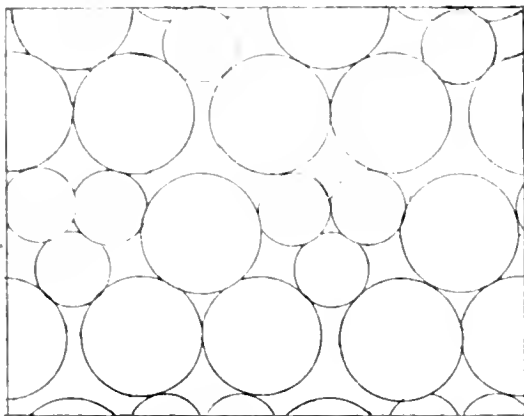


FIG. 7a.

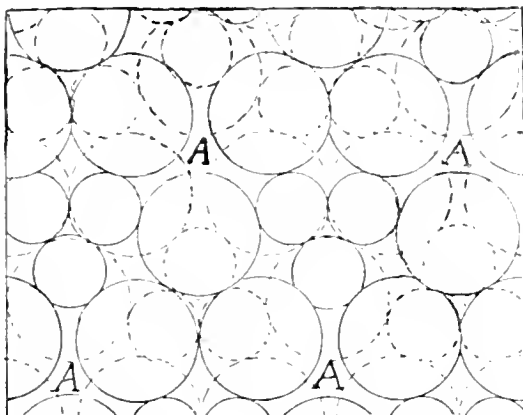


FIG. 7b.

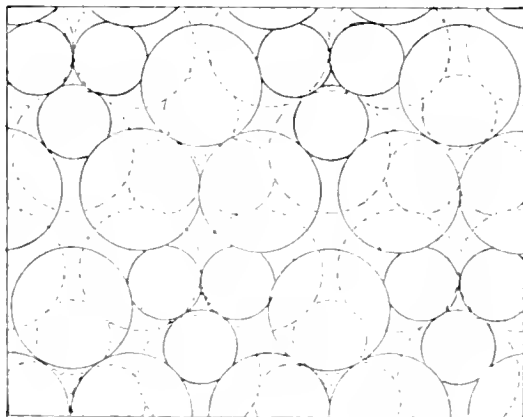
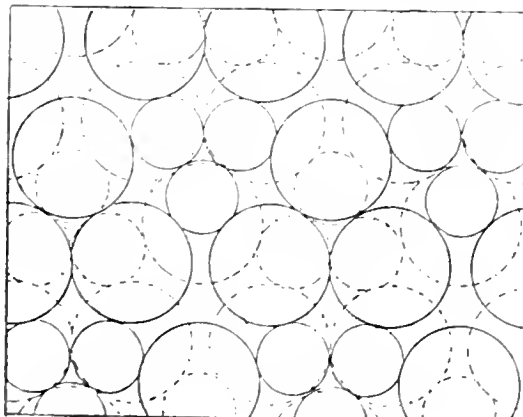


FIG. 7c.



assemblage then consists are connected by coincidence-movements about hexagonal screw axes perpendicular to the plane of the layers (Barlow, *Sci. Proc. Roy. Dublin Soc.*, 1897, 8, 527). From either the cubic or the hexagonal close-packed arrangement one-fourth of the spheres can be symmetrically removed without impairing the symmetry; each layer then presents the appearance shown in Fig. 8, and in both cases the assemblage can be regarded as made up of octahedral groups of six spheres, two layers combining to furnish a single stratum of groups as shown in Fig. 9. The number of cavities being twice that of the octahedral groups, if three smaller spheres, each having one-fourth the volume of a larger sphere, are squeezed into each cavity of an assemblage of either kind, the composition C_nH_n is attained, and since the carbon spheres occur in groups of six, the partitioning yields units of the benzene composition C_6H_6 .

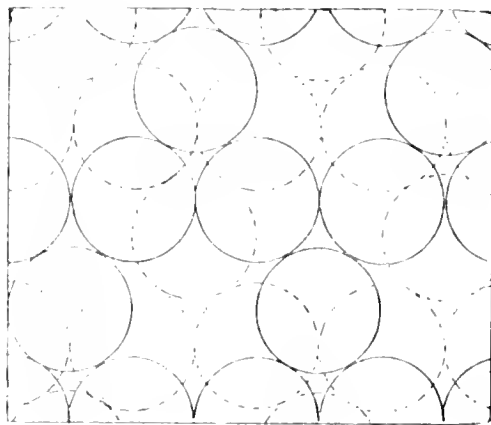
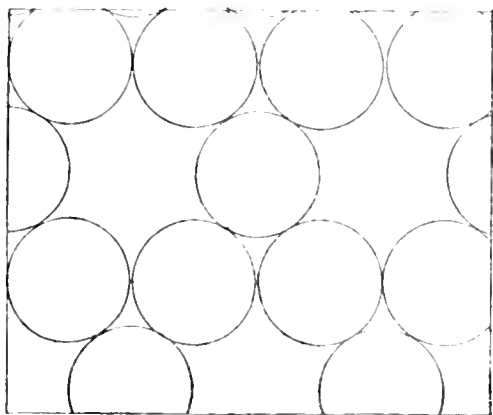
After this replacement of one-fourth of the spheres by sets of three small spheres in either the cubic or the hexagonal assemblage, a comparatively slight distortion or adjustment suffices to re-establish close-packing; the appropriate distortion of the

hexagonal assemblage converts it into the benzene assemblage of Fig. 3, whilst the system derived from the cubic assemblage, by a slight distortion, yields the rhombohedral or nearly rhombohedral assemblage of Figs. 7*a*, *b*, and *c*. In the latter case the distortion consists in a compression in the direction of one of the four trigonal axes, the planes of the triads of small spheres remaining practically parallel to the planes of the layers.

A comparison of the diagrams will show that the benzene assemblage of hexagonal derivation (Fig. 3) and that of cubic derivation (Figs. 7*a*, *b*, and *c*) are geometrically closely related, in addition to being symmetrically partitionable into units of the same marshalling; in both assemblages the smaller spheres are grouped in triads, each group being contained in a cavity surrounded by twelve of the larger spheres, and the three spheres of a group being attached to three

FIG. 8.

FIG. 9.



different benzene complexes. Among the prominent or singular points are found, in each case, the centres of the benzene complexes and the centres resembling them which are situated midway between six large spheres not belonging to the same complex and the centres of the cavities containing the smaller spheres. The other singular points of the two systems do not correspond.

In an undistorted assemblage, retaining complete rhombohedral symmetry, as in that represented in Figs. 7*a*, *b*, and *c*, the ratio of the equivalence parameters x and y corresponding to the x and y of crystalline benzene would be 0.8660 : 1, this being the ratio between the lengths of the side and the perpendicular to the side in an equilateral triangle; the value z would be rather less than in the case of the assemblage for benzene depicted in Fig. 3. The substitution of slightly different halogen spheres for hydrogen spheres in certain of the halogen derivatives of benzene will evidently affect the rhombohedral marshalling and lower the symmetry; the departure from rhombohedral symmetry

may be expected to be somewhat pronounced. The values quoted for the orthorhombic (*O*) and monosymmetric (*M*) benzene halogen derivatives in the appended table, which is calculated from data given by Fels (*Zeit. Kryst. Min.*, 1900, **32**, 358), seem to indicate that the crystalline structure of these substances is one derived from the cubic marshalling of the complexes just described.

	Crystal system.	β .	Multiples Mole- of axial cular ratios vol-		$a : b : c.$	$x : y : z.$
			chosen.	unc.		
1:4-C ₆ H ₄ Cl ₂	M	100°25'	$a/2$	96·4	2·3366:1:1·3920	3·1306:3·6828:2·6457
1:4-C ₆ H ₄ Br ₂	M	98 11½	$a/2$	104·4	2·4720:1:1·3774	3·2274:3·5966:2·6111
1:4-C ₆ H ₄ I ₂	O	90 0	$b/2$	—	0·4342:1:0·3653	3·1402:3·6161:2·6419
1:2:4:5-C ₆ H ₂ Cl ₄ M		99 26	$2c$	116·2	0·9011:1:0·3650	3·2414:3·5852:2·6169

Notwithstanding difference in crystalline system and accompanying differences in the extent to which the assemblages are sheared in the various directions, and the slight differences in the relative volumes of the spheres of influence of hydrogen, chlorine, bromine, and iodine, the respective x , y , and z values agree closely throughout the series.

It will be seen from the foregoing that a close-packed, homogeneous assemblage has been derived which is entirely representative of our chemical and crystallographic knowledge of benzene; also that the crystal symmetry of several of the halogen derivatives of the hydrocarbon is almost identical with that of a close-packed assemblage of the benzene molecular units having the alternative arrangement described. Having thus given a detailed example of the methods of working adopted, it will be convenient to summarise briefly as follows the salient features presented by such close-packed equilibrium assemblages as those depicted.

Any chemical compound can be represented by a close-packed and homogeneously symmetrical assemblage of slightly deformed spheres of the appropriate magnitudes, A , B , C , &c., in which the numerical proportions of the different components are those of the spheres of influence of the corresponding atoms present in the molecule of the compound represented. In order to differentiate between organic substances having the same percentage composition but different molecular weights or constitutions, a number of different close-packed assemblages of the same composition have to be formed, the units of which are different. Thus the several assemblages composed of spheres representing carbon and hydrogen in equal proportion are obtainable which correspond in number and properties to the hydrocarbons of the empirical composition CH, and differ among themselves both in the magnitudes and configurations of the units or molecules into which they are partitionable. One, and only one, configuration of

unit represents acetylene ; another dipropargyl ; and a third, as shown above, represents benzene. Further, the comparison of numbers of close-packed assemblages representing organic compounds reveals the existence in different assemblages of compound groups identical in composition and configuration ; these component groups are the radicles known to organic chemistry, and the persistence of a particular type of structure as an element throughout widely differing assemblages characterises that particular structural element as a radicle. Again, the fragments of the close-packed assemblages which represent different radicles can be classified in homologous or related series according to their composition and symmetry ; the groups representing complex radicles, such as benzyl, benzoyl, acetyl, ethyl, &c., contain particular groups representing simpler radicles, such as phenyl, methyl, &c., precisely in accordance with our knowledge of those complex radicles.

If the substance under consideration is one of known crystalline form, it is found that the general symmetry of the close-packed assemblage is identical with that observed in the corresponding crystal. The axial ratios and interaxial angles of the latter are also compatible with the relative dimensions of the close-packed assemblage ; the correspondence also extends to the optical properties, to the twinning and to any so-called optical anomalies exhibited by the crystalline substance, these being paralleled by corresponding symmetrical structural features of the properly constituted assemblage. In very many cases close-packed assemblages of spheres representing a particular substance can be built up in two or more ways, each being in accordance with the chemical nature of the substance and partitionable into identical chemical molecules. The one of these assemblages can in some cases be distorted symmetrically in such a manner that it passes over into the other, the symmetrical distortion thus enabling a passage from one type of symmetry to the other. The alternative of symmetrical arrangement of the same set of units, whether achieved in this way or not, indicates polymorphism, and the different kinds of crystallographic symmetry actually exhibited by the substance are represented by the types and dimensions of the two or more close-packed assemblages.

Where, in consequence of the presence of the same units or radicles in two assemblages and a similar or partially similar arrangement of them, some of the translations or other dimensions are the same in both assemblages, difficulty is often experienced in detecting the similarity of dimension ; the difficulty is, in many cases, due to the axial directions chosen not corresponding in the two crystalline structures, similar directions not being immediately apparent from an inspection of the crystalline forms ; an instance bearing on this is found in the cases of hexachloro- and hexabromo-benzene, dealt with above. But when this complication does not arise, the relation between polymorphous iso-

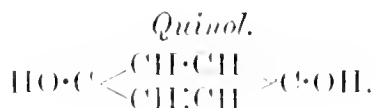
merides is frequently seen to be of a very simple character. This may be illustrated by a comparison of the orthorhombic mineral gerhardtite, $4\text{CuO}, \text{N}_2\text{O}_5, 3\text{H}_2\text{O}$, with the synthetic monosymmetric compound of the same composition, using the crystallographic data by Wells and Penfield (*Zeit. Kryst. Min.*, 1886, 11, 303).



	β .	a	:	b	:	c .	x	:	y	:	z .	Density.
Natural	90°	0.92175	:	1	:	1.1562	3.1858	:	3.4562	:	3.9961	3.426
Synthetic	$85^\circ 27'$	0.9190	:	1	:	1.1402	3.1976	:	3.4791	:	3.9673	3.378

Notwithstanding the difference of crystalline system and of density, it will be seen that relative lengths of corresponding dimensions in the two structures, as indicated by the equivalence parameters $x:y:z$, are almost the same. A slight shear of the orthorhombic structure would bring its symmetry into congruence with that of the monosymmetric one. The monosymmetric mineral eudidymite, exhibiting $a:b:c = 1.7107:1:1.1071$, $\beta = 86^\circ 14' 30''$, and the orthorhombic epididymite with $a:b:c = 1.7274:1:1.0680$, both of which have the composition $\text{NaBeHSi}_3\text{O}_8$, are related in precisely the same manner as the foregoing (Flink, *Zeit. Kryst. Min.*, 1894, 23, 353). Another instance of similar kind is supplied by the rhombohedral and monosymmetric forms of quinol, which are described in detail later (p. 1704).

The previously current views as to the constitution of benzene do not, of course, lend themselves in any way to the detection of a connexion between constitution and crystalline form, and although the discussion of the initial problem has led to a result which agrees so well with the mass of available qualitative and quantitative data that little doubt can survive as to the general accuracy of the solution offered, it is desirable that we should further consolidate our position by the study of a typical set of substitution derivatives of benzene. We therefore proceed to the investigation of the three dihydroxybenzenes, triphenylmethane and its derivatives, triphenylamine, naphthalene, and anthracene, in order to show that, by adhering strictly to the mode of procedure adopted in the case of benzene itself, it is possible to obtain close-packed assemblages of the appropriate spheres whose types of symmetry and relative axial dimensions are in agreement with our chemical and crystallographic knowledge. Although in some cases the arrangement in the actual crystal may be other than that here suggested, it is not probable that this frequently occurs, as it would generally involve the existence of two arrangements for the same molecular units, both very closely packed and both displaying symmetry of structure referable to the same one of the thirty-two crystal classes, and having the same or interconvertible axial dimensions.



Quinol, or *p*-dihydroxybenzene, is dimorphous, and the first modification to which we direct attention is that which crystallises in the rhombohedral system and exhibits $a = 108^{\circ} 4' 36''$; $a:c = 1:0.6591$ (Groth). The occurrence of the high rhombohedral symmetry is of importance, in that it imposes narrow limitations upon the nature of the close-packing of the molecules in the crystal structure and upon the configuration of the molecules themselves. The assemblage appropriate to quinol is derived from the benzene unit or molecule in the following manner.

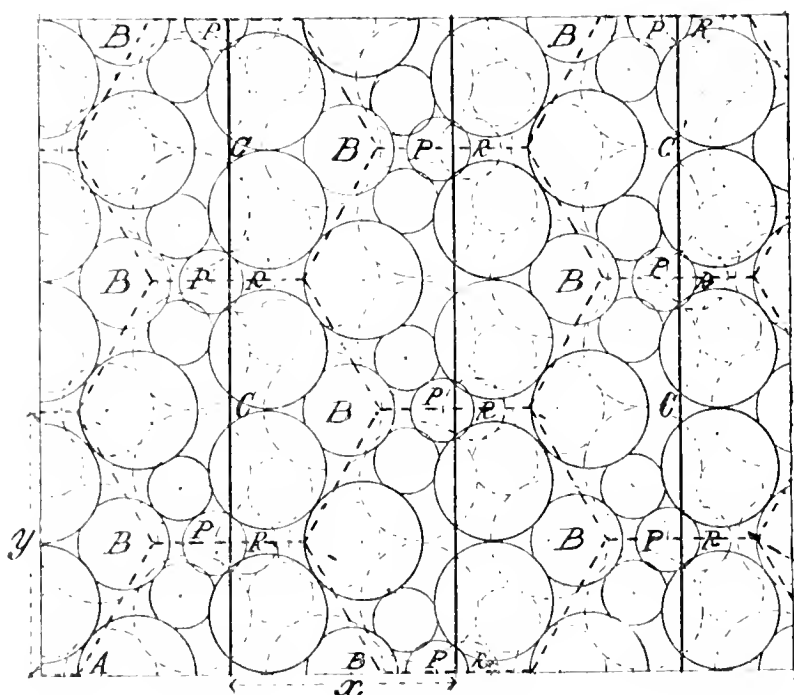
Benzene complexes distorted as in Fig. 3 are arranged in mutual contact and similarly orientated upon the same plane in such a way that the centres of the complexes lie at the knots of an equilaterally triangular network. Triads of small spheres are observable in the plane layer thus obtained, just as in Fig. 3, but the three individual spheres forming a triad are no longer all in contact. Substitute now one sphere of each triad by a sphere of twice its volume, the substituted spheres being similarly situated throughout the plane layer of complexes, and being so selected as to conserve the digonal axis of rotation which passes through the centre of each benzene complex. The introduction of this larger sphere just about suffices to bring it into contact with the two smaller spheres of the same triad, but still leaves in the structure a gap bounded on one side by those two smaller spheres; this gap is filled by the introduction of another hydrogen sphere, which then makes contact, or nearly so, with five spheres of a face layer. This last inserted sphere is rather large for the narrowest part of the gap which it occupies, and will therefore project a little, either above or below the level of the hydrogen spheres; its position can, however, be so adjusted as still to conserve the digonal axes.

The arrangement now arrived at is indicated in Fig. 10, in which the two layers of spheres making up the one layer of complexes are respectively represented by continued and broken lines; the thick straight lines represent the projections of the digonal axes. Each of the broken line hexagonal cells indicated approximately outlines one quinol molecule or one unit of the structure.

Since the plane network formed by the centres of the original benzene complexes becomes in the quinol structure an equilaterally triangular one, successive layers of complexes identical with the first can be built up so that the set of digonal axes found in any one layer is at 120° with the set found in the next layer. The orientation of successive layers thus related is so chosen that the

system forms a series of screw-spiral; corresponding points in the first and fourth layers of complexes having the same projection on the plane parallel to the first plane layer. On thus stacking successive layers, the spheres of any layer may individually move up or down slightly in such a manner as to accommodate the contours of neighbouring layers. As the presence of spheres of different sizes makes the layers of different thicknesses in different parts, it is essential for close-packing that the layers should be so adjusted, one above the other, that thick portions of the one are superposed upon thin portions of the next; this is achieved by the adoption of the spiral arrangement described. The attainment of close-packing will be further assisted

FIG. 10.



because, since the mass consists of elastic deformable spheres and is supposed subject to a general and uniform compression, a slight mutual adjustment of the relative positions of the component spheres will occur so as to produce increased closeness of packing; this change will be probably symmetrical, and therefore unlikely to alter the character of the general symmetry. In the present case it will not be necessary to indicate the precise nature of this adjustment, and the more so, as it consists merely in a slight movement, mostly up or down, of some sphere or spheres with respect to others in the layer. For the sake, however, of clearness, it will be well to state in general terms the nature of this mutual accommodation of the layers of an assemblage one to another, which can occur without the accompaniment of material rearrangement or remarshalling.

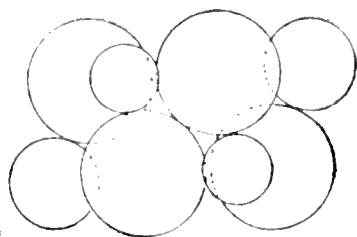
If an assemblage of elastic spheres, mutually in contact and subject to general compression, or some system of mutually repellent centres mechanically equivalent to it, is nearly but not quite closely-packed or in equilibrium, the assemblage will pass to a condition of equilibrium in close-packing by executing small relative mutual adjustments of its parts. And if the original system is either symmetrical or so nearly symmetrical as to be capable of becoming completely so when equilibrium is ultimately reached, the resultant assemblage will be a symmetrical or homogeneous one; in other words, the same conditions of equilibrium will continually repeat themselves throughout it. And when it is considered that the spheres of influence, which, for purposes of simplicity, we are now treating statically, are certainly the seat of great dynamic activity, it must be concluded that the establishment of equilibrium as just indicated will be a very rapid process. The question as to what equilibrium of composition must characterise a system in order that it may be capable of close-packing in homogeneous arrangement is discussed in a later chapter on valency.

It will be seen that the geometrical partitioning of the assemblage shown in Fig. 10 resolves it into units or molecules of the para-constitution, in which the spheres of intermediate size representing oxygen are diametrically opposite each other on a line passing through the centre

of the molecule (Fig. 11). The hydroxylic hydrogen spheres are not shown in Fig. 11, because their precise position is not fixed by the symmetry; it is not immediately apparent what precise course is taken by the walls of the partitioning which separates the assemblage into molecular units.

The assemblage depicted in Fig. 10 as appropriate for quinol possesses trigonal symmetry, and in addition has digonal axes perpendicular to and intersecting the trigonal axes; the digonal axes are those already described, and also an equal number which lie midway between and parallel to them. It is identical in kind with that attributed to quinol on the basis of the goniometrical examination, with the exception that it possesses no centres or planes of symmetry; the assemblage is thus an enantiomorphous one, and is of type 46 or 47 of Barlow. The type of symmetry of the measured crystals of quinol and of the structure described and figured above being identical, with the exception that the indicated enantiomorphism has not been detected, it remains to show that the axial ratios of the crystals are compatible with the dimensions of this structure and that attributed above to benzene.

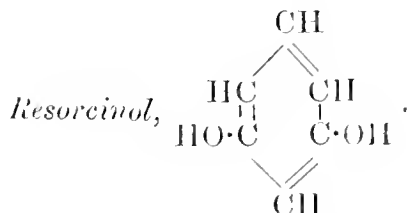
FIG. 11.



On substituting $3a/4$ for a in the axial ratios for quinol, the latter become $a:c=1:0.8788$, and, throwing these into the orthorhombic form of $a:b:c=0.8660:1:0.7610$, and calculating the equivalence parameters, taking the valency volume $W=34$, the values $x:y:z=3.2238:3.7227:2.8330$ are obtained. Fig. 10 is drawn to the same scale as the benzene assemblage, employing these parameters; the value of z is, as it should be, a trifle greater than in the case of the hydrocarbon.

The principal dimensions of the monosymmetric form of quinol become nearly identical with those of the rhombohedral form if the fractions of the axial ratios suggested by Arzruni (*Physik. Chem. d. Kryst.*, 1893, 227) are adopted, for then $a/3:b:c/2=0.8683:1:0.7790$, $\beta=107^\circ$, are obtained. Two of these axial values are identical with those of the rhombohedral form, and the third, namely, the c -value, corresponds to an oblique measurement expressing nearly the same thickness of stratum as is indicated by the corresponding perpendicular axis c in the trigonal form. The equivalence parameters, $x:y:z=3.2526:3.7459:2.9184$, $\beta=107^\circ$, are obtained from the axial data modified as above; in comparing these values with those of the rhombohedral form it should be noted that $2.9184 \times \sin 107^\circ = 2.7909$, a quantity very near to the z -value of 2.7800 for benzene.

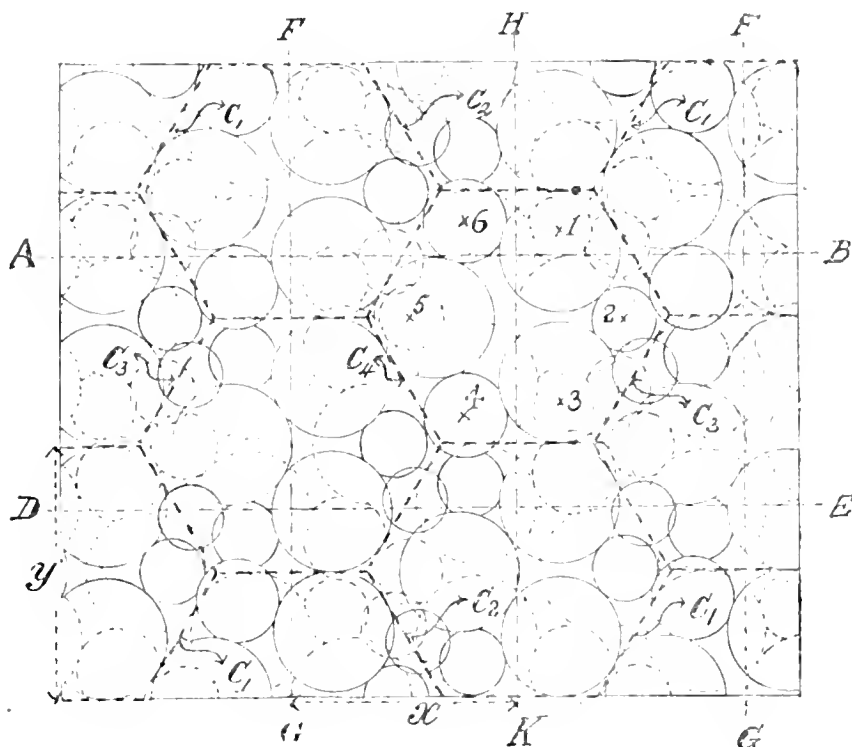
It is suggested that the assemblage of the monosymmetric form of quinol is composed of layers of the same nature as those present in the rhombohedral assemblage depicted in Fig. 10, which therefore applies to both forms, but that the disposition of succeeding layers is different. The arrangement in the case of the rhombohedral form is that derived from the holohedral hexagonal arrangement of the benzene complexes, whilst in the monosymmetric form the layers are so deposited one on the other that a plane of symmetry passes through the centre of each benzene complex perpendicular to the digonal axis. In other words, the two assemblages assigned to quinol precisely parallel the two attributed above to benzene; one of these is found in the crystalline hydrocarbon itself and its perhalogen derivatives, and the other in its di- and tetra-halogen derivatives.



In order to obtain a homogeneous assemblage isomeric with that representing quinol, but in which the two hydroxyl groups are in the meta-positions as in resorcinol, layers differing distinctly,

though not greatly, from those indicated in the former case must be employed. An assemblage representative of the structural features of resorcinol is shown in Fig. 12, in which, as in the case of the quinol assemblage shown in Fig. 10, each considerable gap among the large spheres of a layer is occupied by three of the smallest or hydrogen size and one of the medium or oxygen size. In Fig. 12 the projection of one half of the double layer of spheres or single layer of benzene complexes is represented by broken lines, the other half, which is either above or below the first, being indicated by continuous lines; the exigencies of the packing do not allow of the centres of all the

FIG. 12.



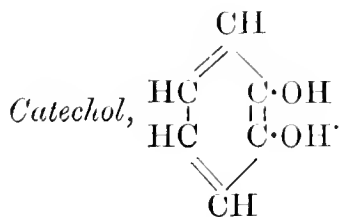
spheres in a layer lying quite in the same plane, and the extent of this deviation is indicated by a slight overlapping in parts of the projection. The hydroxylic hydrogen sphere in particular is, just as with quinol, prevented from attaining the level of the others by being rather large for the narrower parts of the gap into which it must be inserted, and therefore projects above the others.

As before, the assemblage can be geometrically partitioned into hexagonal prisms with identical contents as indicated in the figure; the hexagons are, however, not now regular. The molecule is derived as before by associating, in accordance with the partitioning, a group of spheres of one layer, whose centres are contained within a single prism, with a corresponding group in the layer immediately above or

below, whose centres are contained in the same prism. The exact nature of the attachment of the hydroxylic hydrogen atom is, as in the case of quinol, left undetermined by the symmetry; but, if the centres of these hydrogen atoms lie all slightly above or slightly below the planes of the respective layers, the system possesses digonal screw axes perpendicular to the plane of the diagram through all such points as C_1, C_2, C_3, C_4 , the translation component of which is $z/2$, where z is a translation of the system in a direction perpendicular to the plane of the diagram. Two sets of planes of gliding-symmetry perpendicular to the plane of the diagram are also present, and are marked AB, DE , and FG, HK , in Fig. 12. The symmetry about the digonal axes is manifest if the system formed by the continuous line circles is rotated as a whole through 180° about any one of the points C_1, C_2 , &c., when all its parts come to coincidence with the system formed by the broken line circles.

The system displays hemimorphous orthorhombic symmetry of the type $53B_4$ in Barlow's list and $12a$ of Fedoroff; it is therefore identical in crystallographic symmetry with the crystals of resorcinol which Calderon described as belonging to the hemimorphous orthorhombic system and as having the axial ratios $a:b:c = 0.9123:1:0.5876$. It remains now to show that these axial dimensions are compatible with the figured structure.

On substituting c by $4c/3$ in the axial ratios given above, the values, $a:b:4c/3 = 0.9123:1:0.7835$, are obtained, and, since $W=34$, the equivalence parameters are $x:y:z = 3.3055:3.6233:2.8388$. It is interesting to note that the value z , which represents a translation perpendicular to the plane of Fig. 12, is practically identical with the corresponding value for quinol. The applicability of the above set of axial ratios is shown as before by drawing the figure representing the assemblage to the scale adopted for benzene, using the above equivalence parameters.



Catechol, or *o*-dihydroxybenzene, is monosymmetric with the axial ratios $a:b:c = 1.6086:1:1.0229$, $\beta = 85^\circ 45'$ (Beckenkamp, *Zeit. Kryst. Min.*, 1900, 33, 599). These values may be transposed by writing a_1 for b , b_1 for c , and c_1 for $a/2$, and then become $a_1:b_1:c_1 = 1:1.0229:0.8043$, $\gamma = 85^\circ 45'$; the valency volume, $W=34$, as before, and the equivalence parameters are $x:y:z = 3.4605:3.5398:2.7833$.

The values of y and z thus obtained differ but little from those of benzene, and, in harmony with this, benzene complexes in which the ortho-substitution of two oxygen and two hydrogen spheres for two hydrogen spheres has been made can be fitted together to form columns and walls just as in the case of the benzene assemblage; the walls can be placed at different levels so as to pack together more closely, but their relative positions must not, as is the case with benzene, be such as to produce digonal axes in the directions a and c . If, however, the digonal axis which passes through the middle of each unit taken alone is made the direction of the b -axis in the assemblage, the fitting together of the walls being effected consistently with this, monosymmetric symmetry will result.

The direction of a in the axial ratios stated is possibly ill-chosen, but, premising that the other two axial directions have been correctly located, and that their dimensions are as indicated, a different choice for the direction a would cause no change in the dimensions indicated as the mean thickness of the walls. And thus, the selection of any other axial direction for the a -axis, as according better with the construction of the assemblage, will accord equally well with the constants b and c or x and z . The extent to which one wall is sheared upon the next is in any case probably not the same as in benzene, owing to the conditions being complicated by the changed configuration of the molecular complexes.

Without tracing the precise form of the catechol assemblage, a diagrammatic representation of the symmetry of the system, in which the shear is not taken into account, is given by Fig. 13, which thus shows merely the mutual disposition of the hexagonal cells using the equivalence parameters stated above, and without indicating how the walls are fitted together. The proper sizes of the various spheres on the benzene scale are not employed, but only their correct relative orders of magnitude.

For purposes of comparison it is convenient to resume the data concerning the dihydroxybenzenes in the accompanying table.

	Crystal system.	$a : b : c$	$x : y : z$
Quinol	Rh.	$\alpha = 108^\circ 4' 30''$	$3.2238 : 3.7227 : 2.8330$
„	Mo.	$2.6050 : 1 : 1.5580$	$3.2526 : 3.7459 : 2.9181$
		$\beta = 107^\circ$	
Resorcinol	Or.	$0.9123 : 1 : 0.5876$	$3.3055 : 3.6233 : 2.8388$
Catechol	Mo.	$1.6086 : 1 : 1.0229$	$3.4605 : 3.5398 : 2.7833$
		$\beta = 85^\circ 45'$	

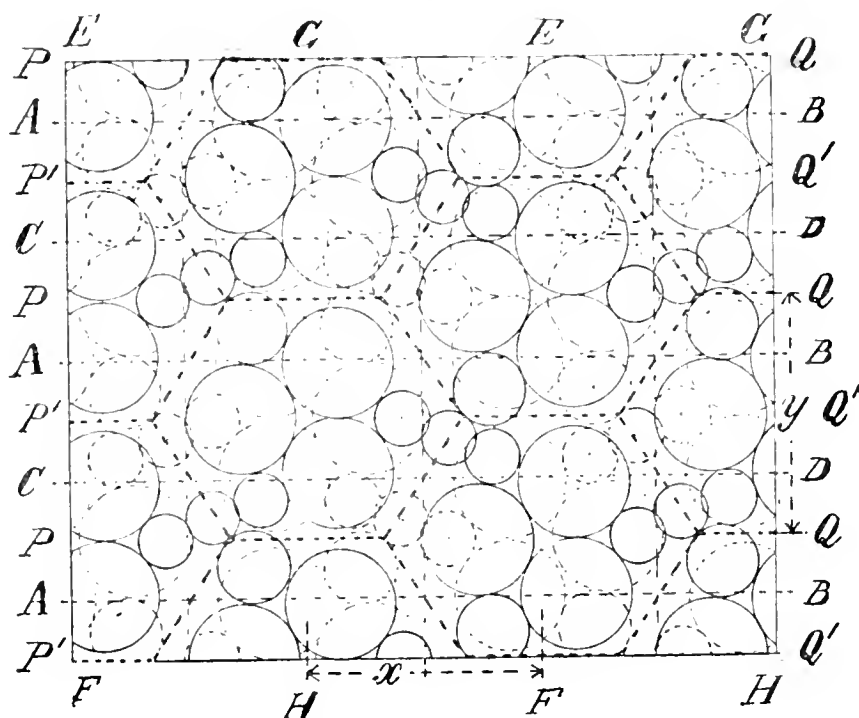
Triphenylmethane, (C₆H₅)₃CH.

The stable modification of triphenylmethane belongs to the hemimorphous orthorhombic system with $a : b : c = 0.5716 : 1 : 0.5867$

(Hintze, *Zeit. Kryst. Min.*, 1884, 9, 546); the labile form is also orthorhombic, and gives $a : b : c = 0.7888 : 1 : 0.6959$ (Groth, *Zeit. Kryst. Min.*, 1881, 5, 478).

An assemblage appropriate for the stable modification of triphenylmethane is derived by disposing three benzene complexes (Fig. 2) triangularly and similarly orientated in the same plane, and replacing the single triad of hydrogen spheres by one sphere of the volume used for carbon in such a way that the latter makes contact with the three complexes and has its centre in the same plane as the other spheres of the layer. The large complex (Fig. 14) now has the composition and constitution of the triphenylmethyl radicle, and a column of such double layers

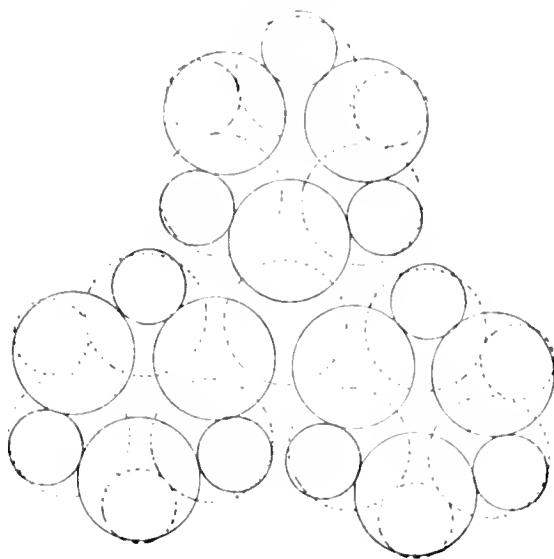
FIG. 13.



can be built up, just as in the case of benzene (Fig. 4), and consists of alternating single layers of two kinds. The packing of the benzene complexes about the central and last inserted carbon sphere in the assemblage can, however, be made closer by effecting a slight adjustment and then inserting an additional set of hydrogen spheres in the numerical proportion of one to each triad of benzene complexes, in the manner shown in Fig. 15. The centre of the last added hydrogen sphere is not exactly in the plane containing the centres of the original spheres, but lies a little above or below that plane, because the available space is rather too constricted in the plane of these centres, whilst there is still space above and below. This condition is indicated by the added hydrogen spheres overlapping their neighbours

slightly, as shown in the plan of the complete structure given in Fig. 16. Each of the last added hydrogen spheres is in contact with either, but not with both, of the methylic carbon atoms belonging to the layers immediately above and below.

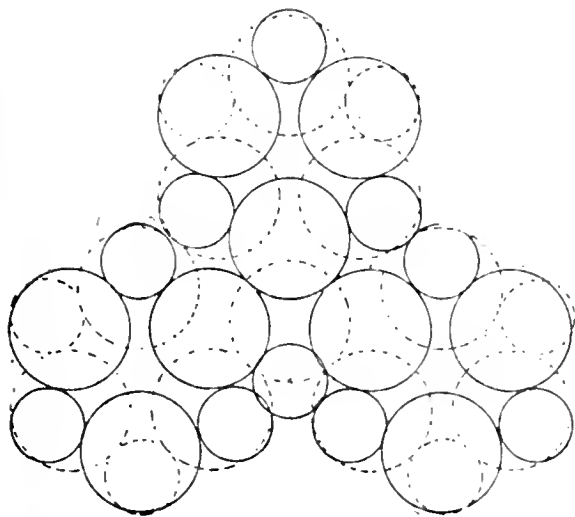
FIG. 14.



After a further slight adjustment which does not involve remarshalling, the composite columnar groups thus constituted can be aggregated so as to form linear serrated walls. Each of these walls, as in the case of resorcinol, consists of alternate single layers of the two kinds represented by continuous and broken line circles. Finally, the walls thus composed can be fitted together and inter-

locked by being placed at different levels, just as in the case of benzene, and in the manner represented in Fig 16. The nature of the geometrical partitioning by means of which the structure is divided into identical molecules is indicated by the thick broken

FIG. 15.



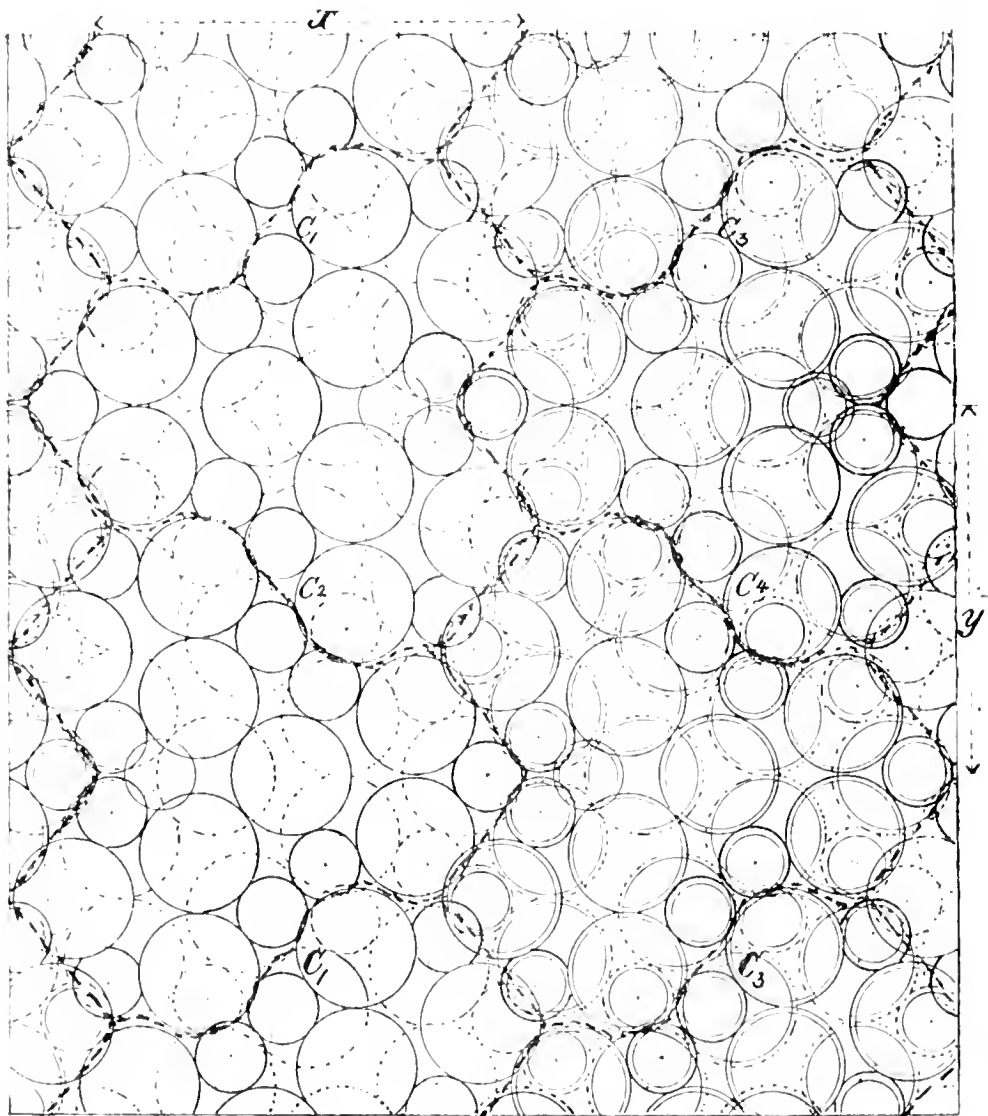
lines in the figure, the slight protrusion of some of the spheres of a molecule beyond the prism boundary of its space-unit being only apparent, and accounted for by the interlocking.

It is not suggested that the diagram presents great accuracy, but it suffices to show the possibility of combining such molecular complexes as those of triphenylmethane so as to form a close-packed assemblage, and, as before, some slight

mutual adjustment of the relative positions diagrammatically indicated is all that is necessary to produce statical equilibrium of such an assemblage as the one proposed. This obviously trivial change can be made so as not to alter the character of the symmetry, and

may, indeed, be regarded as negligible. If the methane hydrogen spheres last inserted in the structure lie all slightly above or slightly below the general planes of their respective layers, digonal axes exist perpendicular to the plane of Fig. 16 through the points marked C_1 , C_2 , C_3 , C_4 ; these are the only ones which can be present. Planes of symmetry exist perpendicular to the plane of the diagram

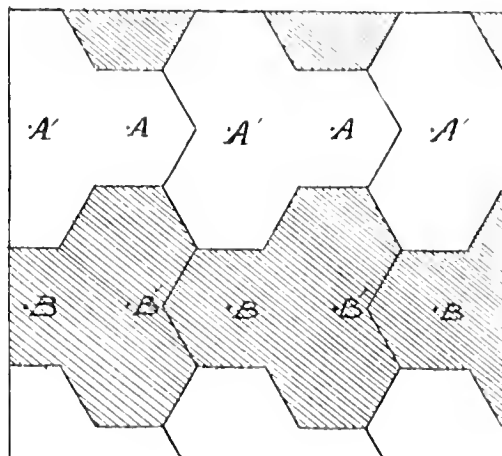
FIG. 16.



and at right angles to the direction of extension of the walls of complexes; they pass midway between the rows of digonal axes. Consequent on the existence of these planes and axes of symmetry, there are also present planes of gliding-symmetry; these are perpendicular to the plane of the diagram, and bisect the walls in the direction of their extension. The direction of the shift in these is perpendicular in the plane of the diagram, namely, in the direction of the axis b or y .

The structure displays hemimorphous orthorhombic symmetry, and is of the type marked $56 B_3$ in Barlow's list and $6\frac{1}{2}$ in that of Fedoroff, and the crystallographic symmetry is thus identical with that assigned by Hintze to the stable form of triphenylmethane. That, in addition to this identity in symmetry, the axial ratios of the hydrocarbon also agree with the dimensions of the assemblage, may be shown as follows: The valency volume of triphenylmethane is 92, and, on taking in the axial ratios given above, $b/2$ and $4c/9$, so that $a:b:c=1.1432:1:0.5216$, the equivalence parameters, $x:y:z=6.1317:5.3637:2.7973$, are obtained; these numbers have been used for drawing Fig. 16 to the same scale as Fig. 3 for benzene. It will be seen that the value $x=6.1317$ is about twice the corresponding value $x=3.1001$ for benzene, and that $z=2.7973$ for triphenylmethane is slightly greater than $z=2.780$ for benzene. The unique position of the methane hydrogen sphere is observable in other cases, and is perhaps accountable for the facility with which this atom is exchanged or replaced.

FIG. 17.



Another arrangement of the same complexes, very similar to the one just described, is possible, which also exhibits hemimorphous orthorhombic symmetry, and which is perhaps the more probable of the two; it is obtained as follows:

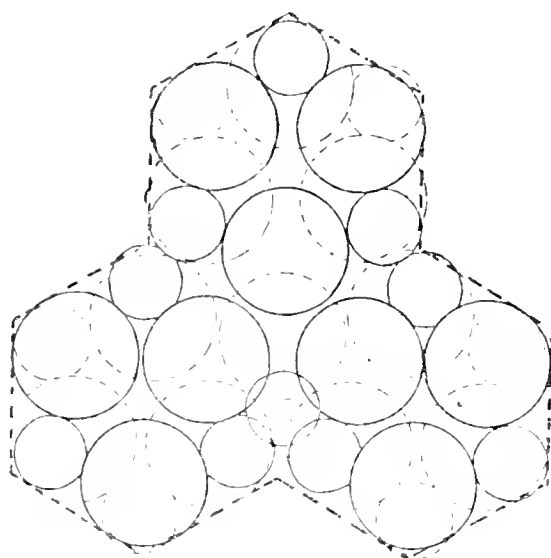
Instead of placing the complexes which lie on the same vertical line in the diagram on the same level, let those lying on the same horizontal line be so placed; the plane assemblage of complexes thus consists of horizontal strings on two levels, as shown diagrammatically in Fig. 17. On laying down succeeding layers, let the orientation of each string be reversed so that diagonal screw axes pass perpendicular to the plane of the diagram through all points A, A', B, B' ; planes of symmetry pass horizontally through the axes A, A', B, B' , and planes of gliding-symmetry pass midway between points A, A' and between points B, B' . The adjustment of the parts in a complex has to be slightly different from that obtaining in the case previously described, in order that the axial ratios may be those stated; the form of complex requisite is that approximately indicated in Fig. 18.

The labile orthorhombic form of triphenylmethane with $a:b:c=0.7888:1:0.6959$ has probably not been so exactly measured as the stable modification, but on selecting the multiples $3b/2$ and $5c/2$,

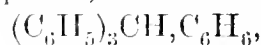
and exchanging a and c , the equivalence parameters, $x:y:z=6.1738:5.3231:2.7995$, result: these agree closely with the corresponding values given for the stable modification. Holohedral orthorhombic symmetry may be attained by the introduction of additional digonal screw axes whose projections are vertical lines in the diagram, and which reverse the orientation of alternate walls of complexes; or the symmetry may be similarly heightened by some other analogous method.

Since the height of one double layer composing a plane of packed triphenylmethane complexes, namely, $z=2.7973$, is about the same as the corresponding dimension, $z=2.780$, in the benzene assemblage, and since the contour and dimensions of one triphenylmethane complex in the assemblage are nearly identical with those of a plane arrange-

FIG. 18.



ment of three benzene complexes, it should be possible to arrange a plane assemblage consisting of triphenylmethane and benzene complexes in equal numbers in close order, and then to form a close-packed assemblage by piling up the layers thus obtained. And it is doubtless as a result of such a process as this that triphenylmethane and benzene yield the crystalline compound,



which is rhombohedral with $a:c=1:2.5565$ (Hintze, *Zeit. Kryst. Min.*, 1884, 9, 545).

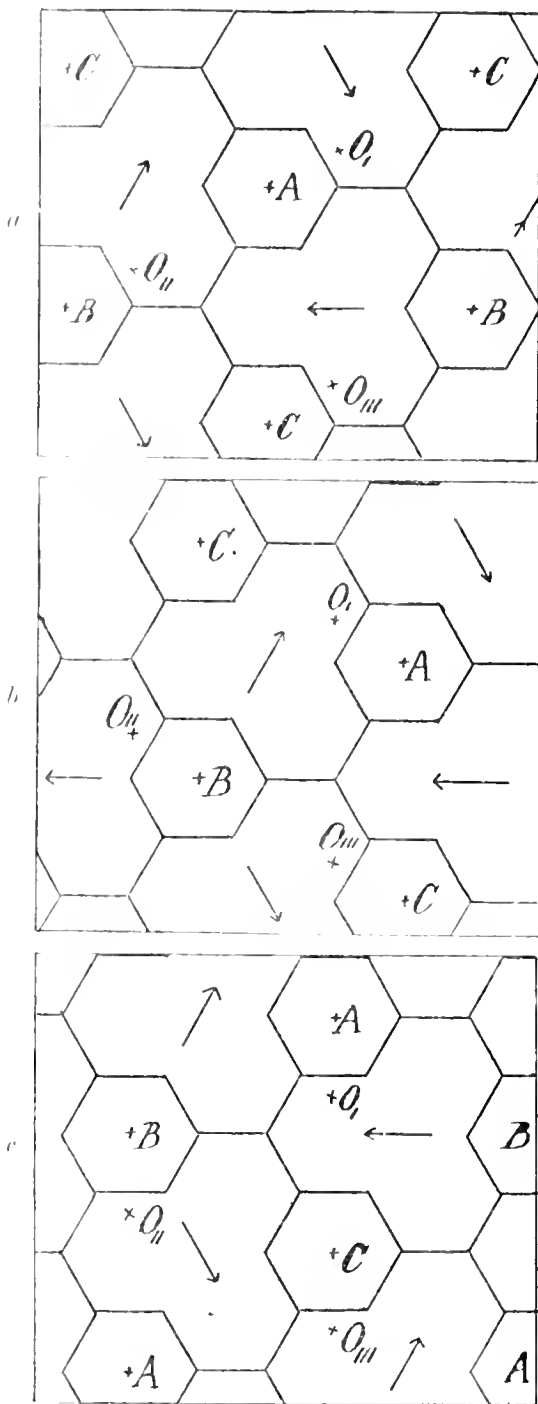
The alternative arrangement of the benzene molecular complexes, that, namely, which is derived from a cubic assemblage and described on p. 1699, is evidently more likely than the rhombic benzene arrangement to lend itself to the derivation of the rhombohedral symmetry of the substance in question. Accordingly, we find that a mixed assemblage composed of equal numbers of triphenylmethane and benzene complexes fulfilling the required conditions is obtainable from the alternative form of benzene arrangement in the following manner:

Partition a layer of benzene complexes of the latter assemblage into a mixture of triplets and single complexes, as indicated diagrammatically in Fig. 19; exchange the triplets for triphenylmethane complexes,

assigning to these the three different orientations possible in a symmetrically distributed manner; the result is a highly symmetrical layer having trigonal symmetry about axes perpendicular to it. Pile such layers one upon the other in such a way that corresponding points such as $A, A, A; B, B, B; C, C, C$, respectively, lie on staircase spirals whose axes are perpendicular to the plane of the diagram through O', O'', O''' ; this would be represented by the superposition of the diagrams a, b , and c . The result will evidently be an assemblage whose dimensions are very compatible with those of the second benzene arrangement. The symmetry of the assemblage depicted is that of the crystal class No. 18, and the data furnished by Hartley and Thomas (this vol., p. 1019) show that the compound $(C_6H_5)_3CH, C_6H_6$, crystallises in class 17 or 18.

In order to show that the axial ratios of the crystalline double compound are in harmony with this view, it must be first pointed out that, dividing c by three, and multiplying throughout by 0.8660, the axial ratios are obtained in orthorhombic form as $a:b:c = 0.8660:1:0.7380$; these figures are almost identical with those of *p*-di-iodobenzene given on p. 1702, namely, $2a:b:2c = 0.8684:1:0.7306$. Now the valency volume, W , of the double compound is $92 + 30 = 122$, and, since its magnitude is about that of four benzene units, the values a and b may each be multiplied by two so as to be about double the corresponding values for the

FIG. 19.



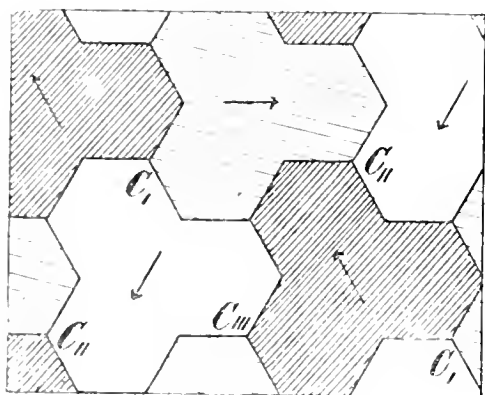
benzene form; the equivalence parameters then become $x:y:z = 6.2824:7.2545:2.6769$. These figures indicate a slight increase in the z value as compared to that of the *p*-di-iodobenzene, namely, $z = 2.6419$; this may be traced to the introduction of the methane residue, CH.

Whilst the character of the triphenylmethane assemblage is such that by a rearrangement of the kind suggested cavities of the shape and size of the benzene unit can be readily produced, complexes of other shapes and sizes could not be so easily intercalated. And in harmony with this it is known that the hydrocarbon does not form addition compounds with fatty substances

nor with homologues of benzene, but does so with thiophen, pyrrole, and aniline, all substances possessing the hexagonal contour of benzene (Hartley and Thomas, *loc. cit.*, 1014). Compatibility of solid contour appears to be a determining factor in the production of other and similar addition compounds. Thus, v. Baeyer found (*Ber.*, 1905, 38, 589) that *p*-tri-iodotriphenylcarbinol forms an addition compound with ben-

zene. The pierates of aromatic hydrocarbons are also probably similarly constituted to the compound, $\text{CH}(\text{C}_6\text{H}_5)_3, \text{C}_6\text{H}_6$, as intercalations of two compatibly shaped groups.

FIG. 20.



Triphenylmethyl Bromide, $(\text{C}_6\text{H}_5)_3\text{CBr}$.

Triphenylmethyl bromide is rhombohedral with $a:c = 0.7843$ (Hintze, *Zeit. Kryst. Min.*, 1884, 9, 549), and on writing the axial ratios in the orthorhombic form of $a:b:c = 0.8660:1:0.7843$, a great resemblance to the constants of benzene becomes apparent. W is 92, and when $2a$ and $3b/2$ are taken in order to make the space-unit commensurate with the molecular complex of triphenylmethane, the equivalence parameters $x:y:z = 6.1671:5.3411:2.7932$, values nearly identical with those for triphenylmethane, are obtained. The manner in which triphenylmethane complexes of the form represented in Fig. 18 can be arranged in rhombohedral symmetry is indicated in Fig. 20; trigonal screw axes occur perpendicular to the plane of the diagram through C_I, C_{II}, C_{III} , and the three different levels at which the complexes lie are indicated by the absence of shading and by the light and dark hatching. The type

of symmetry is that numbered 42 and 43 in Barlow's list and 15 and 16 in that of Sohncke; three different orientations of the complexes are involved, as indicated by the arrows.

Triphenylcarbinol, $(C_6H_5)_3C \cdot OH$.

The replacement of the bromine atom in triphenylmethyl bromide by a hydroxyl group to form triphenylcarbinol involves the insertion into the assemblage of an oxygen sphere of volume two and a hydrogen sphere of volume one in place of the bromine sphere of volume one. A consideration of Fig. 16 shows that but little change need result to the assemblage by this substitution; the oxygen sphere will take the place of the bromine sphere, and the forcing apart of the structure necessary for this will be accompanied by an enlargement of the triangular space below the bromine sphere such as will allow of the insertion of another hydrogen sphere. Some mutual adjustment of parts is required to re-establish close-packing, but the axial dimensions, notwithstanding this, need experience but slight change.

Triphenylcarbinol is rhombohedral with $a : c = 1 = 0.6981$ (Groth, *Zeit. Kryst. Min.*, 1881, 5, 479), and on stating this ratio in the orthorhombic form the value $a : b : c = 0.8660 : 1 : 0.6984$ is obtained; selecting the multiples $4a/3$ and $3c/4$, and calculating the equivalence parameters, the values $x : y : z = 6.2053 : 5.3763 : 2.8162$, are obtained, H being 94; so far as these numbers can be interpreted, it would seem that on substituting hydroxyl for bromine or hydrogen in the corresponding compounds, the structures are enlarged in nearly the same proportion in each of the three directions.

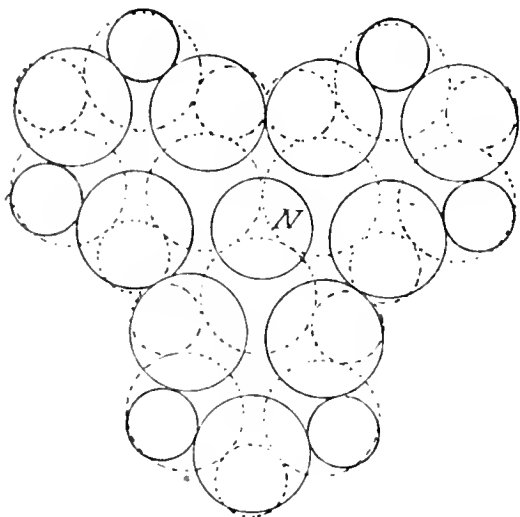
Triphenylacetic Acid, $(C_6H_5)_3C \cdot COOH$.

Triphenylacetic acid is monosymmetric with $a : b : c = 0.8346 : 1 : 0.9250$, $\beta = 42^\circ 34' 30''$ (Groth, *Zeit. Kryst. Min.*, 1881, 5, 483); morphotropically the crystals are nearly rhombohedral, and, for comparison with the substances previously discussed, it is convenient to change the indices of certain forms, making $c, (101)$ and $r, (001)$. We then get $a : b : c = 0.5646 : 1 : 0.6161$, $\beta = 90^\circ 12' 30''$, and on calculating the equivalence parameters from these values, taking $2a$ and $3c/4$, we obtain $x : y : z = 6.5083 : 5.7639 : 2.6657$, H being 100. These valency parameters are quite compatible with those of the series of halogen derivatives of benzene given above, the introduction of the large carboxyl group affecting the parameters x and y and leaving the z value practically the same as in the cases referred to.

Triphenylamine, (C₆H₅)₃N.

If, in the derivation of the complexes and columns representing the triphenylmethyl radicle, the group of three benzenoid hydrogen spheres, instead of being replaced by a carbon sphere of volume four, is replaced by a nitrogen sphere of volume three, close-packing and homogeneity can be retained in accordance with the simple valency law previously briefly stated and without the addition of another hydrogen sphere. The assemblage appropriate to triphenylamine is thus immediately obtained, and consists of complexes of the form shown in Fig. 21, packed together in a manner so similar to that which represents triphenylmethane that a separate figure is unnecessary. Triphenylamine is monosymmetric with $a:b:c=0.9913:1:1.4119$,

FIG. 21.



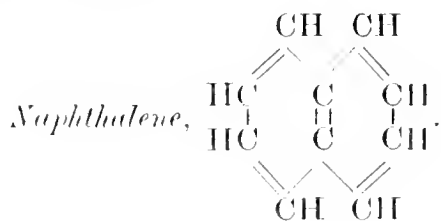
$\beta = 88^{\circ}38'$ (Arzruni, *Zeit. Kryst. Min.*, 1877, 1, 451), $W = 90$, and, on taking $2a$ and $3c/2$, the equivalence parameters $x:y:z = 5.8835:5.5079:2.7781$, are obtained; the z -value is practically that of benzene and triphenylmethane, and the x and y values differ but slightly from those for the latter substance, as would be anticipated; the introduction of the nitrogen sphere necessarily causes less spreading of the complexes in the plane of Fig. 14 than that of a carbon and a hydrogen

sphere. A slight shear given to the triphenylmethane assemblage in the plane containing the directions x and z would degrade the orthorhombic symmetry of that assemblage to the monosymmetric symmetry of triphenylamine.

For purposes of reference it will be convenient to collect the data referring to the above substances in which three phenyl groups are associated in the following table:

Substance.	Crystal system.	Fractions of axial ratios selected.	x : y : z	Auxiliary fractions.
Triphenylmethane :				
Stable form	Or	$b/2, 4c/9$	6.1317 : 5.3637 : 2.7973	$3a/2, 4c/3$
Labile „	„	$3b/2, 5c/2$	6.1738 : 5.3231 : 2.7995	$5c/4,$
$(C_6H_5)_3CH, C_6H_6$	Rh.	$c/3$	6.2824 : 7.2545 : 2.6769	—
Triphenylmethyl bromide	„	$2a, 3b/2$	6.1671 : 5.3411 : 2.7932	none
Triphenylcarbinol	„	$4a/3, 3c/4$	6.2039 : 5.3727 : 2.8143	$2a/3, c/2$
Triphenylacetic acid ..	Mo.	$2a, 3c/4$ $\beta = 90^\circ 12' 30''$	6.5085 : 5.7639 : 2.6657	$2b/3, 4c/3$
Triphenylamine	„	$2a, 3c/2$ $\beta = 88^\circ 38'$	5.8835 : 5.5079 : 2.7781	$4a/3, 3c/4$

Notwithstanding the larger size of the molecular unit containing three phenyl groups, the great resemblance of the corresponding structures to the benzene assemblage indicates that the type of the latter might be closely adhered to in the crystalline forms of these derivatives; and for converting the benzene assemblage into that appropriate to triphenylmethane one axis is multiplied by two and another by three over two. It is of great significance, as supporting the argument concerning fractionation of the axial lengths (p. 1683), that if, in the case of all these triphenyl-derivatives, one axial length is multiplied by two and another by three over two, the further reduction operation which has to be performed on the resulting axial ratios, before they yield equivalence parameters, is much more simple in character than the total reduction operation. This is seen on comparing the last column of the above table, in which is indicated the reduction necessary after one axial length has been multiplied by two and another by three over two in order to secure the conformity of equivalence parameters obtained, with the more complex reduction operation which has to be performed upon the original axial ratios to obtain the same result (column 3).

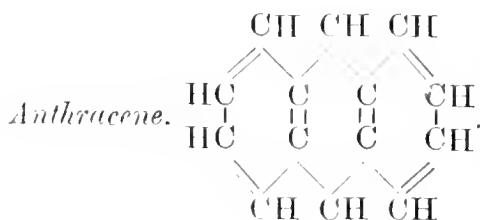
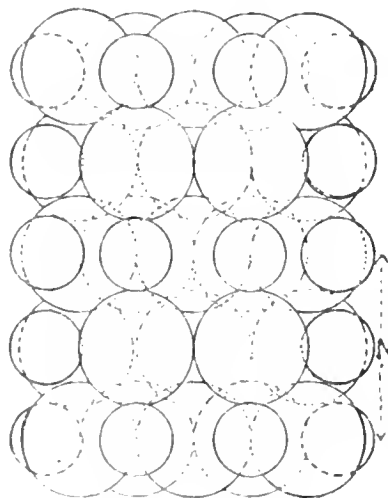
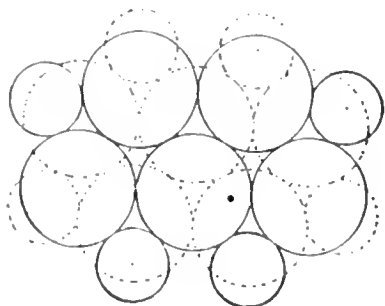


Our knowledge of the chemical constitution of naphthalene is summarised by deriving the configuration of one of the columns in the assemblage representing it from that of benzene (Figs. 1 and 2), in the manner shown in plan and elevation in Fig. 22. A little consideration of this figure will show that the configuration offered fulfils the requirements of a structural formula for naphthalene, as deduced from the isomerism of its derivatives, in just the same way as in the case of benzene.

According to Groth, naphthalene crystallises in the holohedral monosymmetric system showing $a : b : c = 1.3777 : 1 : 1.4364$, $\beta = 57^\circ 11'$, the forms (001), (201), (110), (111), and a perfect cleavage on (001) (Negri, *Zeit. Kryst. Min.*, 1896, 25, 410).

Complexes of the kind shown in the figure can be packed in columns just as can the benzene complexes, and an assemblage is derivable which is in accordance with the crystallographic properties of naphthalene: as, however, we are at present engaged upon the crystallographic examination of a number of simple naphthalene derivatives, we propose to leave the further discussion of the nature of the naphthalene assemblage until this work is completed.

FIG. 22.



The application to the complex representing naphthalene of the process by which that complex was derived from the one representing benzene can be made in two ways, leading to the production of complexes which are in entire harmony with current knowledge of the constitution of anthracene and phenanthrene respectively. The configuration representing anthracene is shown in plan in Fig. 23, and examination will show that it is in agreement with the known isomerism of derivatives of the hydrocarbon. Units of this kind can be packed to form a close-packed assemblage in accordance with the crystal form of anthracene; we shall, however, deal later with the packing of these units in connection with naphthalene.

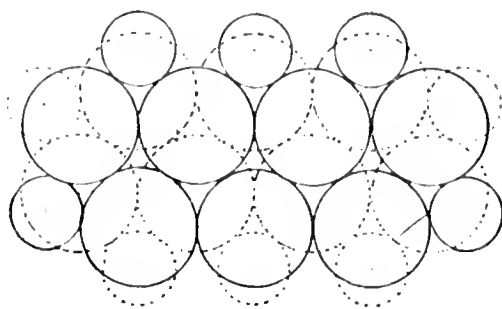
An inspection of the models representing the molecular configurations of the aromatic hydrocarbons, benzene, naphthalene, and anthracene reveals a great resemblance of parts; thus, regarded in one direction they all present the same aspect, that, namely, which is represented in the elevation depicted in Fig. 2*b*. The specific properties associated with the aromatic substances are doubtless attributable to this likeness in configuration. This will naturally also apply to such substances as thiophen, pyridine, &c.

The Nature of Valency.

Having illustrated the way in which chemical substances can be formulated as close-packed assemblages, and having demonstrated that the method has the unique advantage of closely correlating molecular structure and crystalline form, it will be convenient to direct attention to certain well-marked geometrical properties of close-packed assemblages. From the way in which triphenylmethane, triphenylamine, &c., have been derived from benzene, it is clear that some sort of relationship exists between close packing and valency, although the precise nature of that relationship is not immediately obvious.

We have now to show that close-packed assemblages of spheres of different sizes, held in stable equilibrium as described, are characterised by the possession of three general geometrical properties, and to demonstrate that these properties are merely the geometrical expression of chemical valency. The three properties in question refer (1) to equality of valency, (2) to the valency relations of atoms or radicles of different valency volumes, and (3) to multivalency.

FIG. 23.

*On Equi-valency.*

From a homogeneous close-packed assemblage of spheres, similarly environed single spheres, or groups of two,

three, or more, can be removed homogeneously so as to leave a residual set of spheres which, although homogeneous, is no longer close-packed. The cavities which have been produced, being homogeneously arranged, are similar and identically related, and can thus be re-occupied by a different set of identically similar groups of spheres or single spheres. The packing of the new assemblage thus derived can, like that of the original assemblage, be made very close without any remarrying of the unremoved spheres, if such general deformation and local adjustment occur as will adapt the shapes of the cavities to the shapes of the new contents, but leave the cavities of about the same relative volumes as before the process of exchange. Under these conditions and provided the distortion is not extreme, an intimate morphological relation of the nature described later will exist between the original and the derived assemblages.

The essential condition for close-packing is that each sphere of an

assemblage of spheres shall be in actual contact with or in close juxtaposition to a relatively large number of spheres; in other words, that only a small part of that shell-shaped portion of space immediately surrounding any sphere shall consist of interstices. And the provision that the cavities vacated preserve approximately their original magnitude ensures that the framework in which they occur merely suffers such slight alteration in the density of its packing as is involved in the change of shape of the cavities consequent on the latter being packed with fresh contents; in fact, the shell-shaped portion of space immediately surrounding each cavity is about as densely packed with spheres after substitution as before, and consists of the same spheres.

It is possible, however, to retain a high degree of closeness of packing if the removal of spheres as just described is followed by an equivalent introduction of other spheres to fill the vacant cavities. The geometrical property of close-packed homogeneous assemblages which is here concerned may be formally stated in the following terms. If in a close-packed assemblage of spheres, single spheres or groups of two or more, selected homogeneously, are replaced homogeneously by other groups of spheres in such a way that the resulting assemblage is close-packed without resorting to remarshalling, the replacing group is practically of the same relative magnitude as the group replaced, and possesses the same fundamental valency.

This geometrical property of close-packed homogeneous assemblages is the obvious analogue of an important class of observed facts relating to isomorphism, morphotropy, valency, and chemical substitution.

Thus, on replacing in a compound an atom of an element by another belonging to the same group in the periodic system, the resulting compound is ordinarily isomorphous with the first; the two elements of the same group are represented by spheres of atomic influence of so nearly the same size as compared with the sphere volumes of other constituents that the one replaces the other without, in general, leading to a change of crystalline system. It is convenient to show how closely the one sphere of atomic influence must approximate in size to that of an isomorphous element by the following table dealing with the series of alkali sulphates and selenates which have been so accurately measured by Tutton (*Trans.*, 1905, **87**, 1188); the equivalence parameters are calculated on the assumption of the pseudo-hexagonal structure made by Tutton:

	<i>V.</i>	<i>W.</i>	<i>x</i> : <i>y</i> : <i>z</i> .
K_2SO_4	61.91	12	2.2109 : 2.1977 : 2.8463
Rb_2SO_4	73.31	12	2.2049 : 2.1899 : 2.8648
Cs_2SO_4	84.58	12	2.2003 : 2.1826 : 2.8777
K_2SeO_4	71.67	12	2.2207 : 2.2083 : 2.8204
Rb_2SeO_4	79.94	12	2.2147 : 2.1957 : 2.8412
Cs_2SeO_4	91.09	12	2.2112 : 2.1900 : 2.8524

It is observable that slight, though appreciable, disturbances attend the substitution of potassium by rubidium or caesium or of sulphur by selenium. The distortion of the assemblage thus indicated would be produced if the spheres of atomic influence of potassium, rubidium, and caesium, or of sulphur and selenium, differ slightly in relative magnitude. The phenomena observed in connection with isomorphism, of the nature noted above, and especially those of polymorphism, indicate that, under the same external conditions, two elements do not appropriate spheres of atomic influence which bear precisely the same ratio to the molecular magnitude. Further, many facts connected with the relative stability of analogous compounds, such, for instance, as that of the chlorine compounds of the nitrogen group of elements, NCl_3 , PCl_3 , AsCl_3 , &c., lead to a similar conclusion; at the same time, the differences are not of such a magnitude as to lead to a difference of valency or, what is the same thing, not so great as to necessitate a remarrying when an atom of the one replaces an atom of the other element in a compound.

It would seem that for two elements to be isomorphously replaceable one by the other, their spheres of atomic influence must be much more nearly of the same magnitude than if they are merely to possess the same valency. This is distinctly indicated by the more considerable changes produced in the equivalence parameters by the mutual replacement of hydrogen, potassium, and sodium, univalent elements which are not isomorphous; it is illustrated by the following table:

	a : b : c .	Multiples of axial ratios taken.	x : y : z .
Picric acid (orthorhombic) :			
$\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$	0.9370 : 1 : 0.9740		3.5587 : 3.6994 : 3.7981
Potassium picrate (orthorhombic) :			
$\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OK}$	0.9420 : 1 : 1.3520	$3c/4$	3.5238 : 3.7407 : 3.7932
Amidosulphonic acid (orthorhombic) :			
$\text{NH}_2\cdot\text{SO}_3\text{H}$	0.9948 : 1 : 1.1487		2.2933 : 2.3053 : 2.6481
Potassium amidosulphonate (orthorhombic) :			
$\text{NH}_2\cdot\text{SO}_3\text{K}$	0.9944 : 1 : 0.7097	$5c/3$	2.2704 : 2.2832 : 2.7006
Phthalic acid (monosymmetric), $\beta = 86^\circ 21'$:			
$\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$	0.7080 : 1 : 1.3452		2.5801 : 3.6442 : 4.9022
Potassium phthalate (orthorhombic) :			
$\text{C}_6\text{H}_4(\text{CO}_2\text{K})(\text{CO}_2\text{H})$...	0.6705 : 1 : 1.3831	$2a, c/2$	2.5409 : 3.6742 : 4.9272
Sodium phthalate (orthorhombic) :			
$\text{C}_6\text{H}_4(\text{CO}_2\text{Na})(\text{CO}_2\text{H})$...	0.7262 : 1 : 1.4197		2.5756 : 3.5468 : 5.0353

On replacing hydrogen by potassium or sodium, much more deformation of the assemblage occurs than when potassium replaces rubidium or caesium; the incompatibility of pattern between the original and derived assemblages in the former case accounts for the non-formation of isomorphous mixtures between an acid and its alkali salt, or between a potassium and a sodium salt of the same metal. If this is really a true statement of the case, it would be expected that two elements of the same valency, which cannot replace each other isomorphously in simple compounds, might do so in more elaborate complexes, because the distortion produced by replacing one sphere of atomic influence by another markedly different in size would be less considerable in the larger than in the smaller complex. We thus find that whilst the equivalent elements tin, lead, and platinum do not replace each other isomorphously in their simple compounds, they do so in more complex compounds; thus the three salts, $K_2Sn(OH)_6$, $K_2Pb(OH)_6$, and $K_2Pt(OH)_6$, are isomorphous (Zambonini, *Zeit. Kryst. Min.*, 1906, 41, 53).

The change of relative magnitude of the spheres of atomic influence as any vertical column in the periodic table is descended is frequently indicated in the axial ratios of the binary compounds. Thus the axial ratios $a:c$, of the hexagonal minerals, zincite, ZnO , greenockite, CdS , and wurtzite ZnS , are 1:1.6219, 1:1.6218, and 1:1.6004 respectively; this indicates that the spheres of atomic influence of zinc and cadmium, or of sulphur and oxygen, have not the same relative magnitudes, but the identity of the axial ratios of zinc oxide and cadmium sulphide suggests that the relative volumes of the spheres of atomic influence of zinc and cadmium are in the same ratio as are those of oxygen and sulphur.

We may conclude that the geometrical interpretation of the periodic law is possibly that in any vertical column of the periodic classification of the elements the magnitudes of the spheres of atomic influence change slowly and in the same direction as the column is descended; in passing from one vertical column to the next, however, the general magnitude of the spheres of atomic influence changes so considerably as to amount to a change of valency or, in other words, to necessitate remarshalling when an atom belonging to one column is replaced by an atom belonging to another.

One important practical bearing of the first geometrical property is the simple interpretation which it affords of a whole class of morphotropic relations which have hitherto resisted explanation, those, namely, in which a close crystallographic relation subsists between substances derived one from the other by replacing one group by another, dissimilar in form and kind. Thus the following anorthic minerals :

$$a : b : c.$$

Albite, $\text{NaAlSi}_3\text{O}_8$ $0.6335 : 1 : 0.5577$, $\alpha = 94^\circ 3'$, $\beta = 116^\circ 29'$, $\gamma = 88^\circ 9'$

Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$... $0.6347 : 1 : 0.5501$, $\alpha = 93^\circ 13'$, $\beta = 115^\circ 55'$, $\gamma = 91^\circ 12'$

although greatly different in type of composition, are morphotropically so closely related that they form the plagioclases by isomorphous mixture. They have, however, the same valency volume, namely, 32, and by removing from the albite assemblage the group NaSi , of valency volume 5, it can be replaced without remarrying, and indeed with but little disturbance of the crystalline structure, by the group CaAl , of the same valency volume. Similarly,

Olivine, Mg_2SiO_4 , $a : b : c = 0.465 : 1 : 0.586$, and

Chrysoberyl, Al_2BeO_4 , $a : b : c = 0.470 : 1 : 0.680$,

have the same valency volume, exhibit a similar morphotropic similarity, and are derived, one from the other, by the same kind of substitution. A number of cases of isomorphously replaceable groups occurring amongst minerals have been discussed by Prior (*Min. Mag.*, 1903, 13, 217), and all of these appear to be embraced by the conclusions derived above and in the following pages.

It is clear from the foregoing that neither a replaced group or radicle, nor one which replaces, in a homogeneous assemblage, necessarily consists of spheres which are all of the same magnitude. Thus, the nitro-group, NO_2 , can replace the methyl group, CH_3 , in the manner indicated, the valency volume of both being seven. When, as in this case, there is a marked difference in shape between the substituting and substituted groups some considerable discrepancy between the crystal forms is to be expected, although a marked resemblance may still be observed. The orthorhombic substances, aceto-*p*-toluidide, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_3$, and *p*-nitroacetanilide,

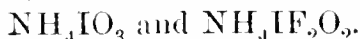


differ in constitution in that the nitro-group of the one is replaced in the other by a methyl group of the same valency volume.

	$a : b : c.$	Multiples of axial ratios taken.	$x : y : z.$
Aceto- <i>p</i> -toluidide	$0.6313 : 1 : 0.3288$		$2.073 : 3.980 : 6.304$
<i>p</i> -Nitroacetanilide ...	$1.0445 : 1 : 0.8889$	$2a, 3\frac{1}{2}c$	$2.001 : 4.178 : 6.223$

The close morphotropic relationships noticed by Zirngiebl (*Zeit. Kryst. Min.*, 1902, 36, 117) between the following pairs of compounds are all similar instances of the application of the first geometrical property of close-packed homogeneous assemblages :

(1) Ammonium iodate, and ammonium fluoriodate,



(2) The stable and labile *o*-sulphobenzoic chlorides,



(3) Phthalic acid, and *o*-sulphobenzoic acid,



(4) Benzoic acid, and benzenesulphonic acid,



(5) Sulphoacetic acid, $\text{CH}_2(\text{CO}_2\text{H})(\text{SO}_3\text{H})$, and methionic acid, $\text{CH}_2(\text{SO}_3\text{H})_2$.

The latter cases are particularly interesting as showing that a carbon atom of valency volume four, is replaceable by a sulphur and an oxygen atom, each of valency volume two, in such a way that the marshalling of the assemblage remains unchanged, and even that corresponding features of the crystalline structures are distinctly recognisable. It is thus indicated that the sulphur in a sulphonic acid is fundamentally bivalent. As will be shown later, the necessity never arises for attributing to sulphur a fundamental valency other than two.

The process of replacing an oxygen and a sulphur sphere, each of volume two, by one carbon sphere of volume four, as involved in certain of the above cases, must be expected to lead to so considerable a change in the shape of the cavity within which the operation is performed as will greatly obscure the morphotropic relations between the two geometrical assemblages; it is thus found that, although the morphotropic relations are distinctly observable, considerable disturbance of the axial ratios and equivalence parameters attends the passage from one to the other of the related compounds.

A word may be said as to the resulting effect when, instead of refilling the gaps produced in a homogeneous assemblage in the manner described, these gaps are closed up by the residual assemblage shrinking together so as to pass to a condition of equilibrium. In order that a homogeneous assemblage of spheres of two or more kinds may exhibit maximum closeness of packing, each component sphere must occur surrounded by a shell of other spheres the density of arrangement throughout which must be a maximum. And if several similarly placed equal spheres are removed from the assemblage and the remaining structure closes up and passes to an equilibrium condition of maximum closeness of packing, it will commonly be found that the component spheres will no longer all be surrounded by shells of spheres equally densely disposed to those composing the original assemblage; and even if the main bulk of the derived assemblage is as densely packed as at first, the assemblage will at isolated points present packing of less density.

The cases quoted above have been selected as illustrations because the simplicity of the crystallographic relationships enables them to be followed quickly, but in most instances the crystallographic relationship is not immediately obvious, being masked by a change of crystalline

symmetry or by an unfavourable choice of axial directions. Notwithstanding this, the relationship is always present, although its detection may involve the kind of investigation used in the foregoing study of benzene, the dihydroxybenzenes, &c. That so considerable a crystallographic difference as that between the rhombohedral and monosymmetric forms of quinol involves no difference in marshalling of the components of the molecule has been already shown, and complication of this nature has in most cases to be dealt with.

Another kind of application of the first geometrical property has been illustrated in the derivation of the assemblage appropriate to triphenylamine from that of benzene (p. 1720), by the symmetrical replacement of groups of three hydrogen spheres each by one nitrogen sphere. We shall show, in a later paper, that the method here used is also of perfectly general application, so that, for instance, the assemblage for tetramethylmethane may be derived from that of methane by the symmetrical replacement of groups of four hydrogen spheres, each by one carbon sphere.

The Relations between Equivalent Radicles of Different Valency Volumes.

The second of the geometrical properties referred to, and which is of importance as indicating the valency relations existing between radicles of the same valency but different valency volumes, may be best realised by the consideration of the following process.

Select a unit—not necessarily a minimum one, but one which includes a considerable number of spheres—in a close-packed homogeneous assemblage of spheres of various magnitudes which is in stable equilibrium under the postulated conditions of external pressure, &c. Partition this assemblage into such units by mere geometrical surfaces, and derive from it an analogous assemblage in the following manner. Withdraw a number of equal and similarly situated spheres, one from each space unit or cell of the partitioning, and, ignoring the partitioning, which has now served its purpose, enlarge similarly the cavities thus left vacant so that they can just contain equal spheres of considerably larger size than those removed; the enlargement necessitated by the introduction of those larger spheres is to be so conducted as to conserve the original marshalling.

The second geometrical property is that, under the above conditions, in order that the modified assemblage, like that from which it was derived, shall be close-packed and homogeneous, some definite number of additional spheres of a particular size must be inserted with the large spheres in each cavity produced in the space unit; the number of the accompanying spheres to be thus introduced is dependent on

their size and on those of the substituting and substituted spheres. The nature of this interdependence of sphere magnitude is experimentally found to be a simple one. If a sphere of volume m (an atom of valency m) is replaced by one of volume $m + n$ (valency $m + n$), one or more additional spheres (atoms) having the total volume n (valency n) must be simultaneously inserted in order that close-packing may be re-established without remarshalling; the bearing of this result on chemical substitution is indicated by the interpolated words. Thus, on replacing a hydrogen atom in the benzene molecule by chlorine, since the substituted and substituting atoms have the same valency and are therefore represented by spheres of about the same relative size, the cavity in the close-packed assemblage vacated by the hydrogen sphere can be so nearly filled by the chlorine sphere, that small deformations or adjustments unaccompanied by remarshalling suffice to restore the close-packing temporarily disturbed by the substitution; the order of the change in the crystallographic dimensions produced by these deformations is indicated by the table of equivalence parameters of benzene and its per-halogen derivatives given on p. 1699. If, however, one hydrogen atom in the benzene molecule is replaced by a carbon atom, the higher valency of the latter necessitates the introduction with it of other atoms, the sum of the valencies of which is three, the difference between the valency of carbon and of hydrogen, if close-packing is to be re-established without remarshalling; thus three hydrogen atoms, giving toluene—one nitrogen atom, giving benzonitrile—or one hydrogen and one oxygen atom, giving benzaldehyde—or some other set of atoms of which the valency volume is three, must be inserted together with the carbon atom, for without this close-packing cannot be secured without remarshalling.

The existence of the second geometrical property may be sufficiently explained for our present purpose in the following manner. Any sphere in a close-packed assemblage is in immediate contact with a number of others, which form, as it were, a shell or envelope about it; if the sphere in question is replaced by one considerably larger, a gap or gaps are formed in the enveloping shell of spheres, which cannot be closed as a result of deformation or adjustment unaccompanied by remarshalling. If a sphere of volume m is replaced by one of volume $m + n$, however, the resulting gap in the enveloping shell can be so filled by a sphere or spheres of the total volume n that the resultant assemblage can regain its original close-packing by the mere operation of slight deformations and adjustments unaccompanied by remarshalling. The great flexibility of structure displayed by close-packed assemblages of spheres naturally assists materially in bringing about this result.

Much of the work detailed in the previous pages, in which it is

shown that the properties of close-packed equilibrium assemblages of spheres are in complete harmony with the crystallographic and constitutive properties of chemically related substances, is so much cumulative evidence of the existence of the geometrical property now under discussion. For, whenever a chemical compound is derived by substitution from some parent substance, the relation between the two compounds is expressible in terms of the valencies of the substituted and substituting groups; and the replacement of an atom by another of higher valency is necessarily accompanied by the introduction of additional atoms in obedience to the valency law.

The mode of operation of the second geometrical property will be seen by a comparison of the methods by which the assemblages for triphenylamine and triphenylmethane were derived (pp. 1711, 1720) from that of benzene. In the former case, by application of the first geometrical property, a group of the three hydrogen spheres of volume three was replaced by a nitrogen sphere of volume three, so that close-packing was retained without remarshalling. But, on forcing a carbon sphere of volume four into the cavity vacated by the group of three hydrogen spheres, the resulting enlargement of the cavity led to the production of a gap in the enveloping shell of spheres, and this proved just large enough to accommodate an additional hydrogen sphere; the latter had, therefore, to be inserted in order that close-packing might be restored without remarshalling. A little consideration will show that the derivation of the dihydroxybenzenes from benzene, and of triphenylcarbinol from triphenylmethane, also involve the application of the second geometrical property.

The cases cited above will suffice for our present purpose, without more formal proof of the accuracy of the way in which the property has been stated. We may now proceed to show that the second geometrical property at once elucidates a number of hitherto very obscure crystallographic relationships, and thereby amass further circumstantial evidence in support of the geometrical interpretation of valency.

The crystalline forms assumed by sodium nitrate and calcium carbonate as calcite are highly distinctive, and are so closely similar as to make it impossible to doubt that the crystal structures and the marshalling are identical; although no explanation has been hitherto available of this identity of crystal structure existing between two substances of such dissimilar type, it now appears that the similarity is a result of the second geometrical property of close-packed homogeneous assemblages. For, if in the rhombohedral structure of crystalline sodium nitrate, NaNO_3 , the univalent sodium atom sphere of volume one is replaced by the bivalent calcium atom sphere of volume two, a gap will be produced in the shell of spheres

enveloping the metallic atom sphere in the assemblage; this can only be filled by the insertion of one additional valency or volume unit if close-packing is to be restored without remarshalling. The additional valency unit is provided by replacing the nitrogen sphere of volume three by a carbon sphere of volume four, and the assemblage, after this double modification, can regain close-packing without undergoing remarshalling. The derived calcium carbonate assemblage retains so closely the marshalling of the original sodium nitrate assemblage that the two exhibit almost identical crystalline forms; the similarity extends even to the unique mode of gliding-twinning, to the cleavage, and to the abnormally high double refraction.

An exactly similar relationship to the above exists between the orthorhombic forms of calcium carbonate and potassium nitrate; the equivalence parameters of all four substances are given in the following table.

	<i>H</i> .		<i>x</i> : <i>y</i> : <i>z</i> .
NaNO ₃ , rhombohedral.....	10	$\alpha = 102^\circ 47'$	2.2092 : 2.2092 : 2.2092
CaCO ₃ , „	12	$\alpha = 101^\circ 55'$	2.3398 : 2.3398 : 2.3398
<i>a</i> : <i>b</i> : <i>c</i> .			
KNO ₃ , orthorhombic	10	0.5910 : 1 : 0.7011	1.7079 : 2.8898 : 2.0260
CaCO ₃ , „	12	0.6224 : 1 : 0.7206	1.8615 : 2.9909 : 2.1553

It is important to notice that in these cases, in passing from the substance of valency volume ten to that of twelve, the structure or assemblage is expanded in all three axial directions; it is not possible to say that the molecular increase affects one axial direction to an appreciably different extent from the others; this should be attributed to the fact that the shapes of the contents of corresponding cells are similar in the cases compared.

Another interesting case arises in connexion with the crystallographic similarity between the monosymmetric alkali salts of methane-disulphonic acid, CH₂(SO₃H)₂, and iminosulphonic acid, NH(SO₃H)₂, which has been pointed out by Zirngiebl (*Zeit. Kryst. Min.*, 1902, **36**, 117). On replacing the tervalent nitrogen atom in iminosulphonic acid by a quadrivalent carbon atom, an additional hydrogen atom has to be simultaneously inserted into the assemblage in order that close-packing without remarshalling may occur. The following data suffice to show that this case is of the same character as that of calcite and sodium nitrate.

	<i>H</i> .	β .	<i>a</i> : <i>b</i> : <i>c</i> .	<i>x</i> : <i>y</i> : <i>z</i> .
CH ₂ (SO ₃ K) ₂	24	89°49'	1.6160 : 1 : 0.9362	4.0604 : 2.5126 : 2.3523
			(take 2 <i>b</i>)	
NH(SO ₃ K) ₂	22	88°41'	1.6636 : 1 : 0.9604	3.9877 : 2.3970 : 2.3021

A somewhat similar relationship holds between the monosymmetric *p*-nitrobenzenesulphonic chloride and amide (Benedicks, *Zeit. Kryst. Min.*, 1903, **37**, 285); the replacement of the chlorine sphere of volume

one by a nitrogen sphere of volume three involves the insertion into the assemblage of two additional hydrogen spheres, forming the sulphonamide, for the purpose of restoring the close-packing without re-marshalling.

	β .	$a : b : c$.	$x : y : z$.
$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Cl}$	105°39'	1.3042 : 1 : 1.1369	3.1955 : 4.9002 : 2.7855
$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2$..	100°12'	0.6591 : 1 : 0.5181	3.3650 : 5.1762 : 2.6833

The case for which data are given in the following table is of importance because all the substances are orthorhombic and the series is four members in length.

	H° .	$a : b : c$.	$x : y : z$.
C_6H_6	30	0.8910 : 1 : 0.7990	3.1010 : 3.4800 : 2.7800
$\text{C}_6\text{H}_5 \cdot \text{NH}_2 \cdot \text{HBr}$	36	0.7230 : 1 : 0.8180	3.2178 : 3.9337 : 2.8441
$\text{C}_6\text{H}_5 \cdot \text{NH}_2 \cdot \text{NBr}_3 \cdot \text{CdBr}_2$..	40	0.7943 : 1 : 0.3944 (take 5/1b, 3c)	3.2268 : 4.4168 : 2.8067
$\text{C}_6\text{H}_5 \cdot \text{NH}_2 \cdot \text{HNO}_3$	41	0.6265 : 1 : 0.5727	3.1126 : 4.9682 : 2.8453

It will be seen that the successive replacement of hydrogen in benzene by NH_2 and the insertion of HBr , and CdBr_2 or HNO_3 , all take place in accordance with the second geometrical property of close-packed assemblages, and that the main effect of the insertion of the various groups falls upon the direction y in the benzene assemblage. The directions x and z in the benzene assemblage are but little changed by the substitutions. The lengthening of one of the three axes which accompanies the substitution of the ammonium bromide residue for hydrogen in benzene is not often observed in cases in which the ammonium radicle replaces an atom of a univalent metal such as potassium; it commonly happens that the axial ratios are practically unchanged by such a substitution as the latter, just as is the case when the group CaC replaces NaN in the rhombohedral sodium nitrate. We purpose dealing later in detail with the relation between salts of ammonium and the alkali metals, and for the present merely call attention to the case of the orthorhombic potassium and ammonium vanadylthiocyanates (Steinmetz, *Zeit. anorg. Chem.*, 1904, **41**, 686), in which the replacement of potassium by ammonium affects two of the equivalence parameters (x and z), leaving the third (y) practically unaltered.

	H° .	$a : b : c$.	$x : y : z$.
$\text{K}_2(\text{VdO})(\text{CNS})_4 \cdot 5\text{H}_2\text{O}$	63	0.9163 : 1 : 0.5469	4.5902 : 5.0095 : 2.7397
$(\text{NH}_4)_2(\text{VdO})(\text{CNS})_4 \cdot 5\text{H}_2\text{O}$..	75	0.9910 : 1 : 0.6070	4.9508 : 4.9957 : 3.0324

It is interesting to notice in connexion with the question of ter- and quinquevalent nitrogen compounds that, whilst the occurrence of benzonitrile, $\text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{N}$, is accounted for on p. 1730, the isomeric phenyl-carbylamine, $\text{C}_6\text{H}_5 \cdot \text{N} \equiv \text{C}$, may be derived, by the application of the first geometrical property, from aniline hydrobromide by replacing

the four univalent atoms associated with the nitrogen atom by a carbon atom.

An instance illustrative of the effect of salt formation is found in the comparison of camphoroxime and its hydrobromide: both these substances are monosymmetric, camphoroxime giving

$$a : b : c = 1.0252 : 1 : 0.6073, \beta = 80^\circ 18'$$

(*Zeit. Kryst. Min.*, 1889, 15, 402), and its hydrobromide,

$$a : b : c = 1.4699 : 1 : 1.0796, \beta = 80^\circ 41'$$

(*Trans.*, 1897, 71, 1048). On transposing the indices of the forms present on the oxime by changing (100) to (101), (101) to (001), (101) to (100), and (110) to (111), and similarly changing in the crystals of the hydrobromide, (001) to (101), (101) to (100), (302) to (001) and (011) to (111), the axial values become comparable and the following results are obtained:

	$a : b : c.$	β	$x : y : z.$
$C_{10}H_{16}:N \cdot OH$	1.2766 : 1 : 1.8571	$\beta = 85^\circ 18'$	3.7935 : 2.9716 : 5.5155
$C_{10}H_{16}:N \cdot OH.HBr..$	1.3356 : 1 : 1.9599	$\beta = 85^\circ 56'$	3.8797 : 2.9048 : 5.6932

The close approximation of the equivalence parameters indicates that not only is the marshalling of the assemblage unchanged by the passage from the oxime to its hydrobromide, but that the dimensions of the assemblage are but slightly altered. The addition of the elements of hydrogen bromide scarcely alters the values x and y , but appreciably increases the value of z .

Orthosulphobenzoic acid, $o\text{-C}_6\text{H}_4(\text{SO}_3\text{H})(\text{CO}_2\text{H})$, yields a stable and a labile acid chloride, to which the constitutions, $o\text{-C}_6\text{H}_4(\text{SO}_2\text{Cl}) \cdot \text{COCl}$ and $o\text{-C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_2 \\ \text{CCl}_2 \end{smallmatrix} \text{O}$, must be attributed; its imide is saccharin, $o\text{-C}_6\text{H}_4 \begin{smallmatrix} \text{SO}_2 \\ \text{CO} \end{smallmatrix} \text{NH}$, to which the axial ratios, $a : b : c = 2.7867 : 1 : 1.7187$, $\beta = 76^\circ 8' 30''$, have been assigned (*Trans.*, 1895, 67, 986). These axial ratios may be transposed by a simple change of indices to $a : b : c = 1.3565 : 1 : 0.4298$, $\beta = 85^\circ 57'$. All these substances are related through the second geometrical property in the manner shown in the following table:

	$a : b : c.$	$\beta.$	Multiples of axial ratios		
			taken.	$x : y : z.$	
Acid	0.6678 : 1 : 1.2074	90°	$4a, 2b$	2.5708 : 3.8496 : 4.6481	
Labile chloride.....	1.8103 : 1 : 2.0997	90°	$2a, 3b$	2.5727 : 3.6773 : 4.4377	
Stable ,,	1.8555 : 1 : 2.0067	$89^\circ 27'$	$2a, 3b$	2.4770 : 3.7025 : 4.5800	
Saccharin	1.3565 : 1 : 0.4298	$85^\circ 57'$	$2b, 3c$	2.5183 : 3.6857 : 4.7521	

The equivalence parameters are related in the same kind of way as those of the similarly related substances dealt with above; but, apart from this, the values for the acid and the labile chloride on the one hand, and for the stable chloride and saccharin on the other, seem

particularly closely related. This would appear to indicate that the labile chloride is the true acid chloride, whilst the stable chloride is the dichloroanhydride of the acid.

The effect on the equivalence parameters of introducing homologous radicles into the molecule is well illustrated by Tutton's measurements (Trans., 1890, 57, 714) of the 1-alkyl-3-diphenyl-5-phenylpyrrolones, having the constitution $\begin{array}{c} \text{CH}\cdot\text{CPh} \\ | \\ \text{CPh}_2\cdot\text{CO} \end{array} > \text{NX}$, in which X represents either methyl, ethyl, or propyl. The methyl and ethyl derivatives are anorthic and isomorphous, and the ethyl derivative crystallises also in monosymmetric forms isomorphous with the propyl compound; the data for these substances are included in the following table:

X.	W.	Crystal system.	$a : b : c.$	$x : y : z.$
Methyl	116	A	$0\cdot9059 : 1 : 0\cdot8695$ $\alpha=79^\circ52', \beta=86^\circ3', \gamma=70^\circ26'$	$4\cdot9092 : 5\cdot4192 : 4\cdot7120$
Ethyl	122	A	$0\cdot9120 : 1 : 0\cdot9524$ $\alpha=78^\circ48', \beta=89^\circ10', \gamma=68^\circ2'$	$4\cdot8928 : 5\cdot3649 : 5\cdot1095$
Ethyl	122	M	$1\cdot6898 : 1 : 1\cdot9579$ $\beta=86^\circ54'$	$5\cdot6273 : 3\cdot3302 : 6\cdot5200$
Propyl	128	M	$1\cdot8060 : 1 : 1\cdot8821$ $\beta=86^\circ17'$	$6\cdot0577 : 3\cdot3542 : 6\cdot3129$

It is seen that in the passage from the methyl to the anorthic ethyl derivative, the x value remains nearly unchanged, the y value diminishes slightly, and the z value increases so as to carry the whole effect of the increased valency volume; similarly, in the passage from the monosymmetric ethyl- to the propyl-derivative, the y value remains almost constant, the z value diminishes slightly, whilst the x value increases so as to bear the effect of the increase of W and the diminution of the z value. No attempt has been made here to bring the anorthic and monosymmetric substances into harmony; but it is clear, from the above changes of the equivalence parameters, that the directions a , b , and c in the anorthic substances are roughly identical with the directions b , c , and a respectively in the monosymmetric compounds and that it would not be difficult to calculate from the data given what directions are absolutely equivalent in the two types of symmetrical assemblage.

As the second geometrical property of close-packed assemblages is obviously a reversible one, further extensions of the method of substitution which it involves can be made. Thus, if one-fourth of the oxygen spheres are homogeneously removed throughout the assemblage of potassium chromate, two additional valency or volume units must also be removed in order that close-packing without remarrying may be possible; when this is done, the residual skeleton, CrO_3 , is obtained. The observed axial ratios for potassium

chromate and chromium trioxide are found to be nearly the same, namely :—

$$\text{K}_2\text{CrO}_4 \dots\dots\dots a:b:c = 0.5695:1:0.7297.$$

$$\text{CrO}_3 \dots\dots\dots a:b:c = 0.6285:1:0.7246.$$

The simplicity of the chemical and crystallographical substitution relations exemplified by the cases dealt with above justifies the hope that before long the relative nature of the assemblages affected by all inorganic compounds will be traceable as a complete scheme exhibiting the relations holding between them.

Multivalency.

The well-known law that the several valencies of multivalent elements in general differ by two or multiples of two has hitherto successfully evaded all attempts to attach to it a physical signification; the recurrence of two and its multiples in this connexion has, however, received a geometrical interpretation in the last few pages. It has been shown that the insertion of an atom of valency $m+1$ into the space vacated in the assemblage by atoms of the total valency m necessitates the simultaneous introduction of an additional atom of valency 1 into the enveloping shell of atoms if the close-packing is to be restored without remarshalling. This process is equivalent to inserting an atom of valency 1 into the space already occupied by an atom of valency m , when the gap produced in the shell enveloping the two atoms must be filled by the insertion of an additional atom of valency volume 1. The atom of valency m will under these conditions function as having the valency $m+2$, although its sphere of influence retains the volume appropriate to an atom of valency m . Similarly, if two atoms of valency 1 are forced into the cavity along with the original atom of valency m , one or more atoms of the total valency volume 2 must be inserted into the enveloping shell for the preservation of close packing without remarshalling, and in this case the original atom of valency m functions as one of valency $m+4$. Thus, the relation between the compounds CsI , CsI_3 , CsI_5 or CsI_7 , and CsI_9 (Abegg and Hamburger, *Zeit. anorg. Chem.*, 1906, **50**, 403) seems clearly indicated; the sphere of atomic influence or the fundamental valency of caesium and of iodine is 1 in each of these compounds. Ammonium chloride, NH_4Cl , also must be regarded as derived by inserting into the ammonia assemblage a monovalent atom of volume 1, when a gap is produced in the shell of spheres originally surrounding the nitrogen sphere which can be filled up so as to restore close-packing without remarshalling by the insertion of another sphere of volume 1; in the ammonium salts the nitrogen atom thus has the fundamental

valency 3. Examples bearing upon this are quoted in connexion with the aniline salts (p. 1733) and the vanadylthiocyanates (p. 1733).

The limitation of the valencies to m , $m+2$, $m+4$, &c., must be expected only when the fundamental valency m , stated as a whole number, expresses closely the volume of the sphere of atomic influence of the element. But it has been already pointed out (p. 1726) as probable that the spheres of atomic influence of elements in the same vertical column of the periodic table change in volume slightly as the column is descended: although the valency, stated as a whole number, remains the same. Discrepancies should therefore arise of the nature illustrated by the following example. Sulphur yields with chlorine the compounds S_2Cl_2 , SCl_2 and SCl_4 , and, in general, as this element exhibits only bi-, quadri- or sexa-valency, it may be concluded that its sphere of atomic influence has very closely the volume 2, compared with that of chlorine as 1, or oxygen as 2. Molybdenum, in the same vertical column, should have a sphere of atomic influence somewhat different from this, and we accordingly find that molybdenum forms the compounds $MoCl_2$, $MoCl_3$, $MoCl_4$ and $MoCl_5$. There seems here a clear indication that, the sphere of atomic influence of chlorine having the volume 1, that of molybdenum is between 2 and 3, for then close-packing might be attained in an assemblage containing twice or thrice as many atoms of chlorine as of molybdenum, and the insertion of two more halogen atoms into each unit of the partitioning in these assemblages in accordance with the second geometrical property would in this event again lead to the production of close-packed assemblages. The fact that the compounds SF_5 and MoF_6 can be formed probably indicates that the sphere of atomic influence of fluorine is slightly smaller than that of chlorine.

In this connexion one necessary consequence of assigning somewhat different volumes to the spheres of atomic influence of two elements of the same valency may be noted. The simple compounds of such elements might differ in type and crystalline form to such an extent that chemical analogies would be difficult to follow; in the more complex compounds, however, built up by the operation of the second geometrical property, the differences in volume of the spheres of influence would exercise less effect than in the simple compounds. It is to be expected, therefore, that very dissimilar elements of the same valency would behave dissimilarly in their simple compounds, but would conform more to the same type in their compounds of considerable molecular complexity. This is illustrated by the fact that the equivalent metals lead and platinum exhibit ordinarily but little analogy, whilst their complex compounds, $K_2Pb(OH)_6$ and $K_2Pt(OH)_6$, are actually isomorphous.

So far as the present inquiry has extended, it has not been found

necessary to attribute to the same element under different conditions of combination spheres of atomic influence of different volumes; that is to say, elements such as sulphur and nitrogen always exhibit the fundamental valencies 2 and 3 respectively, and the higher valencies are merely expressive of the operation of the second geometrical property of close-packed homogeneous assemblages. It remains to be ascertained whether in every case the facts accord with the attributing of one particular fundamental valency to each known element. It is, however, very important that the necessity does not arise for attributing to nitrogen a higher fundamental valency than 3, and that in many per- and proto-metallic salts all known facts accord with the assumption of one, and only one, fundamental valency to the metal.

Thus it will probably be agreed that the formation of the compound KI_3 is not due to potassium becoming trivalent, but to the production of a molecular compound between potassium iodide and iodine. But thalious iodide, THI , which is isomorphous with potassium iodide, can be converted into thallic iodide, THI_3 , which is isomorphous with the compounds RbI_3 and CsI_3 (Wells and Penfield, *Amer. J. Sci.*, 1894, 47, 463; Abegg and Maitland, *Zeit. anorg. Chem.*, 1906, 49, 340), thus :—

RbI_3	$a : b : c = 0.6858 : 1 : 1.1234$
CsI_3	$a : b : c = 0.6824 : 1 : 1.1051$
THI_3	$a : b : c = 0.6828 : 1 : 1.1217$

So that thallic iodide, in which the metal is trivalent, is isomorphous with substances of corresponding molecular composition in which the metal is apparently univalent; the parallel between thallic iodide and the periodides of the alkali metals affords strong presumptive evidence in favour of the explanation of multivalency advanced in the present paper.

There are, as is well known, limitations to the extent to which different elements exhibit multivalency; thus, carbon seems always to be quadrivalent, but sulphur and nitrogen show changeable valency. This difference is traceable to the nature of the partitioning occurring in close-packed assemblages; it is convenient to deal with this particular aspect of the partitioning as a third geometrical property of close-packed homogeneous assemblages. This third property is that, on the introduction, in accordance with the second geometrical property, of additional spheres beyond the numerical proportions required by the fundamental valencies of spheres already present, the resulting close-packed assemblage may be, in general, partitioned in two distinct ways; the one way partitions the assemblage into units representing two different compounds, in each of which the

fundamental valencies alone are involved; the other partitions the assemblage into identical units, and in this case some particular atom of valency m functions as of valency $m+2$ or $m+4$ in accordance with the second geometrical property. It is frequently found practically that only one of the two kinds of partitioning is operative under a given set of conditions, although, in certain cases, both occur simultaneously: thus, the quaternary ammonium salts or ammonium salts exist in solution partly as such, partly as the tertiary amine or ammonia and alkylammonium or hydrogen salt.

The precise nature of the principle which determines whether partitioning of the second kind, into identical units, or of the first kind, into two kinds of units, will occur in any given case cannot yet be determined; it appears to be somewhat akin to the principle which determines polymorphism and largely dependent on temperature conditions, as in the case of ammonium chloride, which at ordinary temperatures is partitionable into units, NH_4Cl , of the one kind, but which at high temperatures is partitionable only into two kinds of units, NH_3 and HCl . The same kind of behaviour is exhibited by some carbon compounds, for triphenylmethyl bromide, under certain conditions, gives a stable periodide, $(\text{C}_6\text{H}_5)_3\text{CBrI}_3$ (*J. Amer. Chem. Soc.*, 1898, 20, 790), analogous to the periodides of ammonium and alkali iodides. The whole question of the magnitude and form of the units produced when a given homogeneous assemblage breaks up, or in other words, the question as to which links break most easily and which survive, is an extremely obscure one. It would seem that as disruption proceeds, small spheres are at a disadvantage as compared with larger ones; perhaps they are moved more violently, and thus their contacts, which are necessarily fewer than those of the larger spheres, are more easily broken. The third geometrical property of close-packed homogeneous assemblages is intimately connected with the whole question of chemical action; and with this we propose to deal later.

The Crystalline and Amorphous States.

The present work indicates that the chemical molecules assume such shapes when arranged in a crystal structure as can be close-packed in homogeneous assemblage; and configurations are assigned to chemical molecules, built up from the spheres of influence of the component atoms which are in entire accordance with our chemical knowledge of the substances considered. A slight difference necessarily exists, however, between the conditions of the molecule in the crystalline state and in an amorphous or unconstrained condition.

Within the crystal the molecule is subject to the action of symmetrically disposed restraining forces identical in kind with those which

endow it with its characteristic shape; the molecule under this action will therefore necessarily experience a definite though slight deformation whilst entering as a unit into a crystalline assemblage. But when the constraining forces are removed by the disintegration of the crystalline structure, it is to be expected that the molecule will assume a rather more symmetrical shape than before. The differences in configuration which may thus arise have been illustrated in the case of benzene; the free and unconstrained molecule will have the structure shown in Fig. 1, and this, in the crystalline structure, assumes the slightly distorted form which is shown packed in the assemblage in Fig. 3.

Apart from such comparatively slight differences as these, the arrangement of the atomic spheres of influence within the molecule must be regarded as nearly identical in both the amorphous and crystalline states, although in the former case the relative situations of the molecules necessarily display more or less heterogeneity; the possible changes in configuration of the molecule are controlled by the condition that, for the substance to preserve its chemical individuality, the marshalling of the parts of the molecule must be the same in all states.

Even in liquids, however, many indications are given that the molecules, from time to time, and from place to place, transitorily assume a homogeneous arrangement throughout tracts which, on a scale of molecular dimensions, are of considerable extent. The doubly-refracting liquids, or so-called liquid crystals, which now form a large class of substances, can only have their origin in wholesale homogeneity of arrangement throughout spaces of molecularly great volumes. Much of the uniformity and symmetry characterising the chemical behaviour of fluid substances can be explained by assuming the existence of this fragmentary homogeneity of arrangement, liable though it must be to continual destruction and reconstitution. The well-known influence of surfaces and of catalytic agents upon chemical action can be easily formulated as due to an arranging effect produced by the surface or catalyst leading to the transitory formation of a complex assemblage which immediately undergoes partitioning into two distinct assemblages in accordance with the third geometrical property of close-packed assemblages.

It must be concluded that, in crystals, the arranging process without which crystallisation cannot occur precedes the act of solidification, a film being present at the surface of the growing crystal which, although not yet solidified, is, owing to the presence of the symmetrically-constituted surface, homogeneously arranged like the substance of the solid crystal. This film will, in general, be of microscopic thin-

ness, although thick when regarded molecularly. The process of crystallisation involves not only the complete homogeneous arrangement of the molecules, but incidentally also their deformation, and this deformation will naturally differ in extent in different substances; the varying amount of deformation which has to be effected in the molecules of different substances during crystallisation may well be a responsible factor in determining the very different speeds of crystallisation observed amongst chemical substances.

The Crystalline Forms of the Elements.

During the present investigation no occasion has arisen for discriminating between the forces which hold the parts of the molecule together and those as a result of which the separate molecules are held together. That such a necessity actually exists is indicated by the fact that those elements, such as sulphur, which are most liable to allotropy occur in several crystalline modifications of low symmetry, whilst most of the others are obtainable only in crystalline modifications of high symmetry. In the cases of crystalline elements, which are at present regarded as composed of identical atoms, it is conceivable that the nature of the packing may be modified by the existence of grouping of the identical spheres of influence of the atoms so as to form molecular aggregates.

Thus, there are two distinct ways in which the closest-packed cubic assemblage of equal spheres can be partitioned into tetrahedral groups of four spheres. In the one partitioned assemblage all the groups are found similarly orientated, whilst in the other one half of the groups display an orientation opposite to that of the remaining half. If a nucleus is formed of the latter arrangement, which has the higher symmetry of partitioning, and this nucleus is caused to grow in accordance with the former or less symmetrically partitioned arrangement, twinning of the mass is brought about which precisely simulates the twinning of diamond (compare Sollas, *Proc. Roy. Soc.*, 1901, 67, 493 and Barlow, *Sci. Proc. Dub. Roy. Soc.*, 1897, 8, 542).

The crystallographic properties of diamond are thus capable of explanation on the assumption that the molecule consists of four atoms tetrahedrally arranged.

Groups of eighteen equal spheres representing carbon atoms can, however, also be built up by the stacking together in trigonal symmetry of three groups of six, each arranged as in benzene; the arrangement is that of the nine spheres, *a*, in one plane of Fig. 24 associated with the nine spheres marked in dotted circles in the figure, and in which the three benzenoid carbon complexes are grouped about

the blackened triangular segment. The graphic formula of such a complex is that of the triple naphthalene ring, and the complexes may be close-packed as indicated in the figure, in which the letters, *a*, *b*, *c*, *d*, *e*, *f*, and *g* refer to the carbon spheres composing one layer of different groups. The assemblage has rhombohedral symmetry, and is thus compatible with the rhombohedral or pseudo-rhombohedral crystalline symmetry of graphite, and an assemblage partitioned into these 18-membered groups might on oxidation be expected to yield mellitic and oxalic acids just as does charcoal and also, with previous formation of graphitic acid, graphite. This suggestion does not, however, without some additional hypothesis, throw any light on the low density of graphite as compared with diamond.

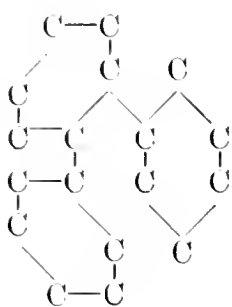
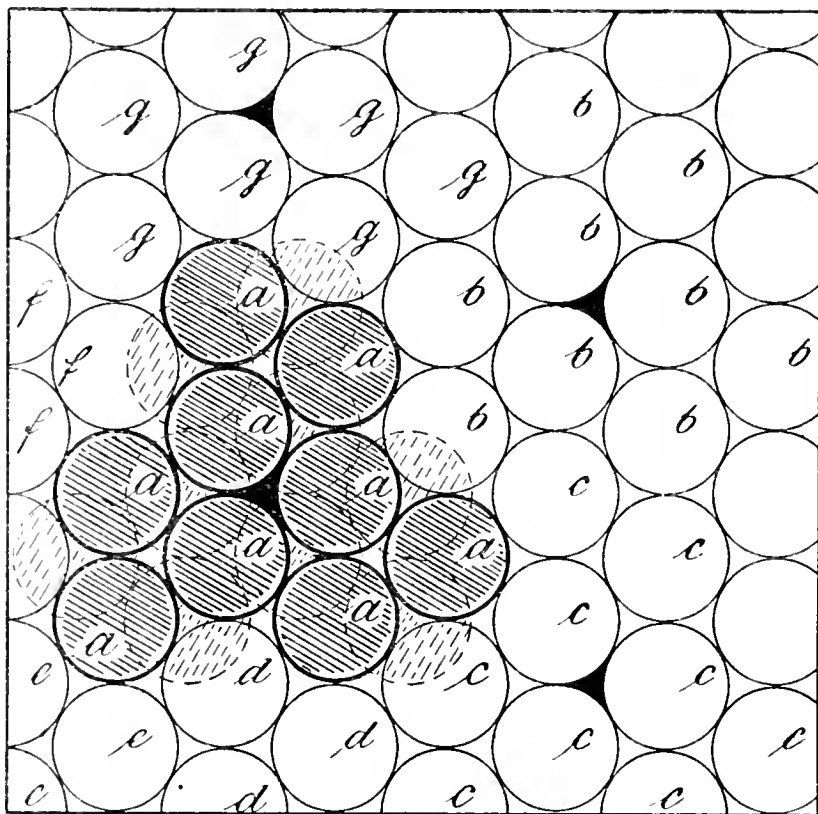


FIG. 21.



Other ways of partitioning a cubic closest-packed assemblage of equal spheres may perhaps also find parallels among the elements; for example, that into groups of eight spheres arranged rhombohedrally. Thus the molecule of sulphur apparently contains 8 atoms (Beckmann, *Zeit. anorg. Chem.*, 1906, 51, 96), and certain of the crystalline modifications of this element exhibit axial ratios which indicate that

they probably originate from some distortion of a cubic arrangement. The monosymmetric fourth modification of sulphur, with $a:b:c = 0.99575:1:0.99983$, $\beta = 84^\circ 14'$ (Muthmann, *Zeit. Kryst. Min.*, 1890, 17, 345), approximates very closely to cubic symmetry.

Conclusion.

Before concluding this paper, it is desirable, for the sake of clearness, briefly to indicate further results which have been obtained, and which we hope shortly to publish in detail.

In one of the homogeneous assemblages of spheres, each representing a carbon atom, one-half of the spheres can be homogeneously replaced, each by four hydrogen spheres; the substituted assemblage is then partitionable into units or cells of the composition CH_4 , and having the tetrahedral marshalling attributed to methane by van't Hoff and Le Bel. If in this methane assemblage one hydrogen sphere is removed symmetrically from each cell or unit of the partitioning, and close-packing restored by shrinking the assemblage together, the subsequent partitioning resolves the assemblage into units of the composition C_2H_6 , each having the marshalling attributed to ethane by van't Hoff and Le Bel. By the further removal of hydrogen spheres and the re-establishment of close packing by the process of closing-up, homogeneous assemblages representative in number and characteristics of all the normal paraffins can be derived, and by appropriate substitutions effected in these assemblages arrangements entirely representative of all the other open chain paraffins can be deduced.

If, in the ethane assemblage, a hydrogen sphere is removed from each methyl group and the assemblage shrunk together in a particular symmetrical manner so as to close up the cavities, an assemblage is produced which may be partitioned into units of the composition C_2H_4 ; the units have the plane configuration attributed by Wislicenus to ethylene, and the assemblage is characterised by geometrical peculiarities representative of unsaturation or the presence of an ethylenic bond. From this assemblage others can be derived by substitution equal in number, and corresponding in properties, to the open chain olefines. The further removal of hydrogen spheres from the ethylene assemblage leads to the production of an assemblage representing acetylene, and this by appropriate substitution can be converted into others representing the homologues of acetylene. These assemblages exhibit a geometrical peculiarity representative of the presence of a triple or acetylenic bond.

Although the crystalline forms of the aliphatic hydrocarbons are unknown, ample crystallographic data relating to simple fatty compounds are available, and with the aid of these the conclusions briefly

described above have been verified. The geometrical peculiarities which are the analogues of an ethylenic and an acetylenic bond suggest that the spheres between which the double or triple bond is operative are not closely surrounded by other spheres, and that when a carbon sphere is in a state of saturated combination the shell of spheres enveloping it will be found to have a maximum density of packing.

The authors' thanks are due to the Committee of the Municipal School of Technology for permitting the blocks illustrating this paper to be made in the school, and to Messrs. Chas. W. Gamble and R. B. Fishenden, of the Photographic and Printing Crafts Department, for the care with which they have carried out the work.

MUNICIPAL SCHOOL OF TECHNOLOGY,
VICTORIA UNIVERSITY OF MANCHESTER.

CLXIX.—*Optically Active Dihydrophthalic Acid.*

By ALLEN NEVILLE, B.Sc.

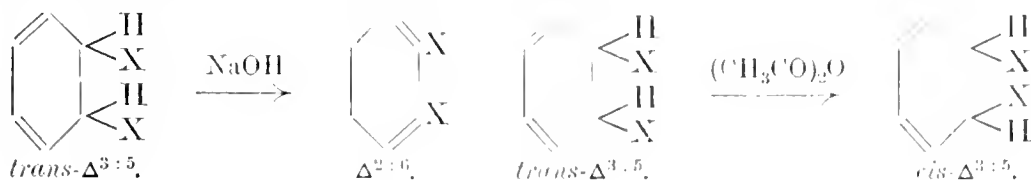
OF the six structurally isomeric dihydrophthalic acids which are theoretically possible, four have been prepared by Baeyer (*Annalen*, 1892, 269, 145), and have had certain formulæ assigned to them. Whilst there is little, if any, doubt as to the correctness of these formulæ, anything in the nature of extra proof is, of course, welcome, and it seemed possible to supply this by seeing if the acids to which Baeyer ascribed a formula containing an asymmetric carbon atom, could be resolved into their optically active isomerides.

Two only of the acids contained such atoms, and one, the $\Delta^{2:4}$ -acid, had already been resolved by Proost (*Ber.*, 1894, 27, 3185), by the crystallisation of its strychnine hydrogen salt.

There remained the $\Delta^{3:5}$ -acid which exists in a *trans*- and *cis*-modification, each containing two asymmetric carbon atoms, and which bear to one another the same relation as racemic and mesotartaric acids, that is, the former only should be capable of being resolved into optically active isomerides. This has been done; the *trans*-acid giving two active isomerides on crystallising the strychnine hydrogen salt, these isomerides having $[\alpha]_D$ 126°.

Baeyer stated (*loc. cit.*) that when treated with sodium hydroxide the *trans*- $\Delta^{3:5}$ -acid was converted into the $\Delta^{2:0}$ -form, and when treated with

acetic anhydride passed into the *cis*- $\Delta^{3:5}$ -modification, according to the following scheme:



As neither of these forms contains an asymmetric carbon atom, the optical activity ought to be destroyed by treatment with these reagents. This was shown to take place in both cases, the change from one modification to the other proving to be a unimolecular reaction under the conditions of the experiment. These results furnish confirmation of the formulæ assigned by Baeyer to the different forms of dihydrophthalic acid.

trans- $\Delta^{3:5}$ -Dihydrophthalic Acid.

This substance was prepared by the method described by Baeyer. Three per cent. sodium amalgam (400 grams) and 50 per cent. acetic acid (60 c.c.) are added in small portions at a time, with constant stirring, to a well cooled solution of phthalic acid (20 grams) and sodium acetate (33 grams) in water (200 c.c.). When the reaction is over the solution is mixed with 20 per cent. sulphuric acid (50 c.c.), kept until the sodium sulphate has separated, and the acid then precipitated with dilute sulphuric acid and recrystallised as quickly as possible from boiling water; it melts at 210° .

l-Strychnine Hydrogen *trans*- $\Delta^{3:5}$ -Dihydrophthalate,

The dihydrophthalic acid (1 mol.) was dissolved in boiling alcohol, and to the solution was gradually added finely powdered strychnine (1 mol). After a short time the strychnine dissolved and, on cooling, the strychnine hydrogen salt separated in rosettes of hard, short needles. This substance is fairly soluble in chloroform, slightly so in alcohol, and insoluble in water or ether. It melts above 280° , and does not lose weight at 100° .

0.2665 gave 12.5 c.c. moist nitrogen at 16° and 770 mm. $N = 5.53$.

$\text{C}_{23}\text{H}_{30}\text{O}_6\text{N}_2$ requires $N = 5.57$ per cent.

The following polarimetric observations* were made after one crystallisation from alcohol:

0.4902, made up to 20 c.c. with chloroform, gave $\alpha = 0.58^\circ$; whence $[\alpha]_D = 11.83^\circ$ and $[M]_D = 59.38^\circ$.

* All observations were made in a 2-dm. tube.

0.1976, made up to 25 c.c. with chloroform, gave $\alpha - 0.20^\circ$; whence $[\alpha]_D - 12.65^\circ$ and $[M]_D - 63.50^\circ$.

l-Strychnine Hydrogen l-trans- $\Delta^{3:5}$ -Dihydrophthalate.

When the racemic salt described above is fractionally crystallised from alcohol five or six times, the *l*-B-*l*-A-salt is obtained in a pure state, as is shown by consecutive crystallisations, giving fractions with a constant rotation. The separation of this salt from the alcohol is very slow, and proper separation does not take place if means be taken to hasten it. The salt crystallises in rosettes of hard, short needles which melt at about 272° with decomposition. It is soluble in chloroform, sparingly so in alcohol, and insoluble in water or ether. The crystals do not lose weight at 100° .

0.2511 gave 11.8 c.c. moist nitrogen at 16° and 770 mm. $N = 5.55$.

$C_{29}H_{30}O_6N_2$ requires $N = 5.57$ per cent.

The pure *l*-B-*l*-A-salt has a rotation about zero and it is curious that this should be so, inasmuch as both its acid and basic constituents are strongly levorotatory.

The pure salt was finely ground, suspended in dilute sulphuric acid, and the dihydrophthalic acid extracted with ether. The ether was dried and evaporated, when the pure *levo*-acid remained. Although one never obtains the whole of the acid in this way, the use of alkali for decomposing the salt was found to be impossible as the acid is so readily transformed.

l-trans- $\Delta^{3:5}$ -Dihydrophthalic Acid.

This acid, obtained by the method described above, crystallises from water in hard, stout needles. It is readily soluble in ether or chloroform, and insoluble in water. It melts at 122° , and does not lose weight when heated at 100° .

0.2003 gave 0.4199 CO_2 and 0.0870 H_2O . $C = 57.16$; $H = 4.82$.

$C_8H_6O_4$ requires $C = 57.14$; $H = 4.76$ per cent.

The following determinations of rotatory power were made:

0.2723, made up to 25 c.c. with absolute alcohol, gave $\alpha - 2.75^\circ$; whence $[\alpha]_D - 126.24^\circ$ and $[M]_D - 212.41^\circ$.

0.2521, made up to 25 c.c. with absolute alcohol, gave $\alpha - 2.53^\circ$; whence $[\alpha]_D - 125.44^\circ$ and $[M]_D - 210.74^\circ$.

0.2215, made up to 25 c.c. with chloroform, gave $\alpha - 2.48^\circ$; whence $[\alpha]_D - 139.95^\circ$ and $[M]_D - 235.11^\circ$.

Whilst the acid undergoes almost no conversion into the *cis*-modification when suspended in water or dilute acid in the cold, hot solutions change it to the other modification. This is shown by the following figures, the rotation of the acid being taken after successive crystallisations from water.

Number of crystallisations	1.	2.	3.	4.	5.
$[\alpha]_D$ in alcohol	126.51	115.12	110.17	103.53	98.21

On boiling for about six hours continuously, no optical activity could be detected, and the acid separating out had a melting point of 215° , showing that the acid had been transformed to the $\Delta^{2:6}$ -isomeride. An accurate measurement of the rate of change was then made by exactly neutralising the acid with sodium hydroxide, and keeping the aqueous solution of the sodium salt at 97° in a water-bath.

0.5 gram of the acid was neutralised with sodium hydroxide and made up to 25 c.c. with water. It was then kept constant at 97° and occasionally cooled down and a rotation taken.

Time in hours.	Observed rotation.	$K = 1/t \log C_0/C_t$.
0.00	5.05	—
0.47	4.65	0.0762
1.60	3.82	0.0757
2.70	3.15	0.0759
4.00	2.51	0.0759
7.10	1.16	0.0758
	Mean	$K = 0.0759$

This shows that the transformation proceeds as a unimolecular reaction.

Far more rapid is the change which takes place when an excess of sodium hydroxide is used, the acid under these conditions being most unstable. This will be seen in the following experiment.

0.4525 gram of the acid was neutralised with sodium hydroxide, and 5 c.c. of *N*/10 sodium hydroxide added in excess. The whole was then made up to 25 c.c. and kept at 50° .

Time in minutes.	Observed rotation.	$K = 1/t \log C_0/C_t$.
0	4.57	—
7	4.12	0.0061
18	3.43	0.0069
27	2.97	0.0069
45	2.25	0.0068
57	1.88	0.0067
	Mean	$K = 0.0067$

The acid recovered from this experiment and the previous one was optically inactive, and melted after purification at 215° ; it was therefore the $\Delta^{2:6}$ -acid.

When the *l trans*- $\Delta^{3:5}$ -dihydronaphthoic acid was warmed with acetic anhydride, and subsequently treated as described by Baeyer, the *cis*- $\Delta^{3:5}$ -modification, melting at 174° , was obtained, which was, of course, optically inactive.

l-Strychnine Hydrogen d-trans- $\Delta^{3:5}$ -Dihydrophthalate.

The salt recovered from the mother liquors after the *l-B-l-A*-salt had crystallised out, did not crystallise well, and remained partly viscous after prolonged desiccation. The most soluble portions only were therefore taken and decomposed as described for the *l-B-l-A*-salt.

d-trans- $\Delta^{3:5}$ -Dihydrophthalic Acid.

This substance, obtained on decomposing the above-mentioned salt, is similar in all respects to the *laevo*-isomeride. It crystallises from water in hard, stout needles, is soluble in alcohol, fairly so in ether or chloroform, and melts at 121° .

The following determinations of rotatory power were made.

0.2012, made up to 25 c.c. with absolute alcohol, gave $\alpha + 2.02^{\circ}$; whence $[\alpha]_D + 125.49^{\circ}$ and $[M]_D + 210.82^{\circ}$.

0.1872, made up to 25 c.c. with chloroform, gave $\alpha + 2.09^{\circ}$; whence $[\alpha]_D + 139.77^{\circ}$ and $[M]_D + 234.87^{\circ}$.

On analysis it gave the following result:

0.1574 gave 0.3299 CO_2 and 0.0684 H_2O . $\text{C} = 57.12$; $\text{H} = 4.81$.

$\text{C}_8\text{H}_8\text{O}_4$ requires $\text{C} = 57.14$; $\text{H} = 4.76$ per cent.

On heating with water or dilute alkali, the acid is transformed into the $\Delta^{2:6}$ -variety in an exactly similar manner to the *l*-isomeride, but sufficient material was not available for quantitative experiments.

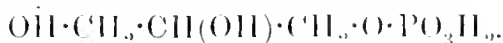
A mixture made by dissolving equal quantities of the *d*- and *l*-isomerides in alcohol, and evaporating the solution to dryness, gave, after purification, the racemic acid melting at 210° .

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CLXX.—*The Relation between Natural and Synthetical Glycerolphosphoric Acids. Part II.*

By FRANK TUTIN and ARCHIE CECIL OSBORN HANN.

WILLSTÄTTER and Lüdecke (*Ber.*, 1904, **37**, 3753) have described the preparation of some salts of a levorotatory glycerolphosphoric acid obtained from egg-lecithin, from which they concluded that the natural glycerolphosphoric acid has the unsymmetrical configuration



They also prepared the synthetical acid by heating together glycerol and phosphoric acid, and claimed to have found essential differences between the barium and calcium salts of the product thus obtained and the corresponding salts of the natural acid, not only with respect to solubility, but especially in the composition of the preparations when dried by heat (*loc. cit.*).

In an account of an investigation by Dr. Power and one of us (*Trans.*, 1905, **87**, 249), it was shown that the above-mentioned differences in composition observed by Willstätter and Lüdecke were due to the fact that their synthetical salts were not pure, but were contaminated with salts of the di-ester, $\text{C}_3\text{H}_5(\text{OH})\text{<O>PO}\cdot\text{OH}$. It was also stated that "the observation of Willstätter and Lüdecke that the glycerolphosphoric acid from lecithin possessed optical activity, although certainly proving the presence of the unsymmetrical acid in the preparation, does not necessarily exclude the possibility that some of the symmetrical acid was also present." Furthermore, that "the same possibility naturally exists with respect to the homogeneity of the synthetical acid."

With the endeavour definitely to ascertain the nature of the natural and synthetical glycerolphosphoric acids, the present authors have

synthesised the unsymmetrical, or α -acid, $\begin{array}{c} \text{CH}_2\cdot\text{O}\cdot\text{PO}_3\text{H}_2 \\ | \\ \text{CH}\cdot\text{OH} \\ | \\ \text{CH}_2\cdot\text{OH} \end{array}$, and the sym-

metrical, or β -acid, $\begin{array}{c} \text{CH}_2\cdot\text{OH} \\ | \\ \text{CH}\cdot\text{O}\cdot\text{PO}_3\text{H}_2 \\ | \\ \text{CH}_2\cdot\text{OH} \end{array}$, and compared the barium and brucine

salts of these compounds, on the one hand with the corresponding salts of the glycerolphosphoric acid prepared from glycerol and phosphoric acid* and, on the other, with those of the racemised acid from egg-lecithin.†

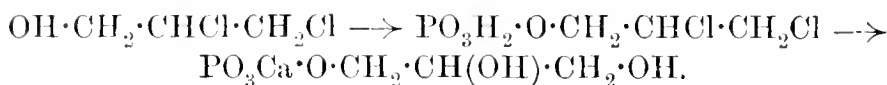
* Subsequently referred to as the "synthetical acid."

† Subsequently referred to as the "natural acid."

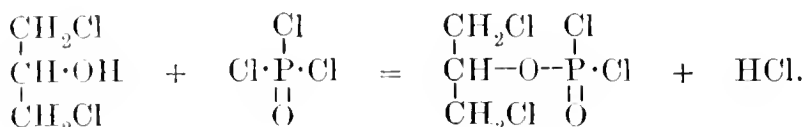
The synthetical glycerylphosphoric acid was prepared from glycerol and phosphoric acid under such conditions as are known to give only the mono-ester (compare Power and Tutin, *Trans.*, 1905, **87**, 249).

The racemised natural acid was prepared in the form of its barium salt by the hydrolysis of lecithin with hot baryta solution. The latter substance was obtained from the yolk of egg by Bergell's method (*Ber.*, 1900, **33**, 2584) and purified by the recrystallisation of its cadmium chloride compound (compare Willstätter and Lüdecke, *loc. cit.*).

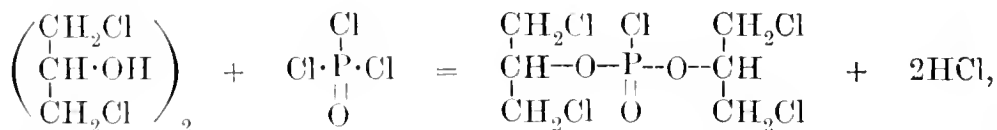
For the preparation of the pure α - and β -glycerylphosphoric acids, the two dichlorohydrins were employed. β -Dichlorohydrin was found to esterify to a small extent when heated with phosphoric acid, and when the resulting product was hydrolysed with milk of lime the calcium salt of α -glycerylphosphoric acid was obtained:



A similar method of procedure was found to be inapplicable in the case of α -dichlorohydrin, as this compound undergoes no esterification when heated with phosphoric acid. Since it had previously been observed that glycerylphosphoric acid could be obtained by the action of phosphoryl chloride on glycerol and subsequent hydrolysis of the product, it was anticipated that if α -dichlorohydrin were treated with this acid chloride a reaction would take place according to the equation:



This, however, is not the case, for when α -dichlorohydrin is treated with phosphoryl chloride at the ordinary temperature no action occurs, but at higher temperatures it was found that a reaction takes place according to the following equation:



and the resulting product, when hydrolysed with milk of lime, yielded calcium β -diglycerylphosphate, $([(\text{CH}_2\cdot\text{OH})_2\cdot\text{CH}\cdot\text{O}]_2\cdot\text{PO}_2)_2\text{Ca}$ (m. p. 249—250°). This compound crystallises from water with $13\text{H}_2\text{O}$, and is soluble in all the usual organic solvents with the exception of light petroleum.*

* It may incidentally be noted that this fact affords conclusive proof that the "di-ester" which is produced when glycerol and phosphoric acid are heated together at a somewhat high temperature (compare Power and Tutin, *loc. cit.*) consists of one or

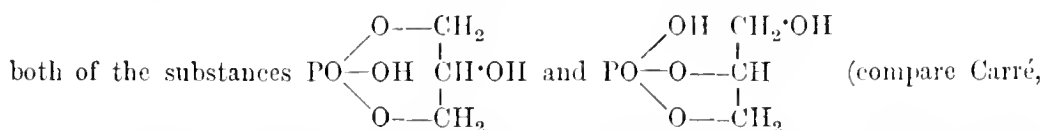
When β -diglycerolphosphoric acid was boiled with water, it was found that hydrolysis slowly took place, giving the desired β -glycerolphosphoric acid, $(\text{CH}_2\cdot\text{OH})_2\cdot\text{CH}\cdot\text{O}\cdot\text{PO}_3\text{H}_2$.

The fact that the barium and brucine salts of these four preparations of glycerolphosphoric acid differ in composition and in many of their properties will be seen from the following table :

<i>Barium Salts.</i>				
	α -Glyceryl-phosphate.	β -Glyceryl-phosphate.	Natural glyceryl-phosphate.	Synthetical glyceryl-phosphate.
Appearance	Well-defined leaflets	Quite amorphous	Leaflets, but not nearly so well defined as the α -salt	Granular powder
Percentage of H_2O in air-dried salt	1.0	5.1	2.4	2.5
Solubility in water at 17°	One part in 26.6	One part in 36.8	One part in 13.9	One part in 53.7

<i>Brucine Salts.</i>				
	α -Glyceryl-phosphate.	β -Glyceryl-phosphate.	Natural glyceryl-phosphate.	Synthetical glyceryl-phosphate.
Appearance	Needles	Needles	Needles	Needles
Water of crystallisation	9 molecules	$11\frac{1}{2}$ molecules	$6\frac{1}{2}$ molecules	7 molecules
M. p. of dried salt ...	$157\text{--}158^\circ$	$157\text{--}158^\circ$	$158\text{--}159^\circ$	$158\text{--}159^\circ$
Optical rotation :				
In water	$[\alpha]_D - 25.3^\circ$	$[\alpha]_D - 23.9^\circ$	$[\alpha]_D - 23.9^\circ$	$[\alpha]_D - 24.6^\circ$
In alcohol	$[\alpha]_D - 32.5^\circ$	$[\alpha]_D - 28.1^\circ$	$[\alpha]_D - 27.9^\circ$	$[\alpha]_D - 28.2^\circ$

It will be seen from the above results that the natural and synthetical glycerolphosphoric acids are not identical. Moreover, neither of them consists of the pure α - or β -acid ; but, as has previously been mentioned, the natural acid must consist, in part at least, of the α - or unsymmetrical acid. Natural glycerolphosphoric acid is therefore a mixture of the α - and β -acids. As the synthetical acid is not identical with either of the pure isomerides, it may be concluded that this preparation is also a mixture of the α - and β -acids. It must, however, be admitted that the results obtained are somewhat anomalous, and do not permit of a ready explanation. For instance, if the barium salts of the natural and synthetical acids are both mixtures of the salts of



Compt. rend., 1903, **137**, 1070), and not the diglyceryl ester, $(\text{C}_3\text{H}_7\text{O}_3)_2\cdot\text{PO}_2\text{H}$ (compare Adrian and Trillat, *J. Pharm.*, 1898, **7**, 226), as the salts of the above-mentioned "di-ester" are insoluble in alcohol.

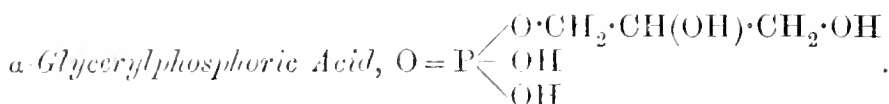
the α - and β -acids, it is difficult to see why one should be more readily, and the other more sparingly, soluble than the salts of either of the pure acids. Furthermore, with regard to the brucine salts, it would not be expected that the amount of water of crystallisation contained in those two which are mixtures would be less than that contained in either of the constituents of these mixtures when in their pure state.

The values obtained for the specific rotations of the brucine salts are recorded, for inasmuch as the structure of the acid radicle is different in the salts of the α - and β -acids, it was to be anticipated that they would exhibit a difference in rotatory power in alcoholic solution. The values obtained for the specific rotations in aqueous solution should, of course, only differ within the limits of experimental error.

Although both the natural and synthetical glycerylphosphoric acids appear to be mixtures, there was no indication that any separation could be effected by the crystallisation of their salts.

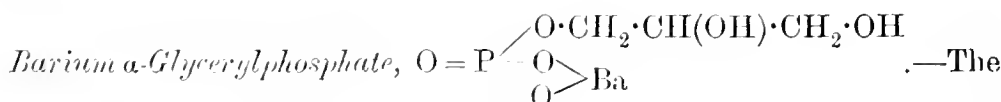
It may thus be concluded from the results of this investigation that the natural and the synthetical glycerylphosphoric acids are differently constituted mixtures of the α - and β -acids.

EXPERIMENTAL.



For this experiment, β -dichlorohydrin was prepared according to the method of Hübner and Müller (*Annalen*, 1871, **159**, 179), by chlorinating dry allyl alcohol (b. p. 96—97°). The fractionated product boiled at 179—180°, and on analysis was found to be pure.

One molecular proportion of β -dichlorohydrin and one and a half molecular proportions of crystallised phosphoric acid were heated together in a paraffin bath for eight hours at 150—155°. The brown, oily product was then poured into an excess of milk of lime, and the mixture boiled for two hours. The liquid was cooled and filtered, the filtrate deprived of the excess of lime by means of carbon dioxide, and again filtered. On evaporation, *calcium α -glycerylphosphate* separated in colourless, glistening crystals; it was freed from calcium chloride by precipitating with alcohol, and collected on a filter. About 3 grams of crude calcium salt were obtained from 40 grams of β -dichlorohydrin.



crude calcium salt obtained as above was dissolved in water, the liquid rendered alkaline with ammonia, and the calcium precipitated and

removed as oxalate. An excess of barium hydroxide solution was added to the filtrate, and the liquid boiled until free from ammonia. After cooling, the excess of baryta was removed by means of carbon dioxide, and the filtered solution evaporated to a small bulk. The *barium α -glycerylphosphate* which separated was recrystallised from water, when it was obtained in glistening leaflets. This salt, like the barium salts of the other preparations of glycerylphosphoric acid, dissolves more sparingly in hot than in cold water.

0.4975 of air-dried salt, when heated at 125° , lost 0.0652 H_2O .
 $\text{H}_2\text{O} = 1.0$.

$\text{C}_3\text{H}_7\text{O}_6\text{PBa}, \frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 2.8$ per cent.

0.4923, dried at 125° , gave 0.3722 BaSO_4 . Ba = 44.5.

$\text{C}_3\text{H}_7\text{O}_6\text{PBa}$ requires Ba = 44.6 per cent.

The solubilities of this and succeeding barium salts were determined by parallel experiments, conducted at the same time, in the following manner. A quantity of the pure salt was placed in a small stoppered bottle and mechanically shaken for eleven hours with about 15 c.c. of water. The temperature of the liquid was 17° . A weighed quantity of the filtered solution was then evaporated to dryness on a water-bath, and the residue weighed. 6.6122 of the solution gave on evaporation 0.2484 of residue, therefore one part of the salt is contained in 26.6 parts of solution.

Brucine α -Glycerylphosphate, $\text{O} = \text{P} \begin{cases} \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH} \\ \text{OH}, \text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \\ \text{OH}, \text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \end{cases}$ —The brucine

salt of α -glycerylphosphoric acid, as well as the brucine salts subsequently described, was prepared by precipitating exactly a solution of the respective barium salt with a solution of brucine sulphate, the barium sulphate being removed by filtration. *Brucine α -glycerylphosphate* readily crystallises from water in rosettes of needles, which, after drying at 100° , melt at 157 — 158° .

0.3074 of air-dried salt, when dried at 100° , lost 0.0443 H_2O .
 $\text{H}_2\text{O} = 14.4$.

In order to ascertain whether the amount of water of crystallisation was a constant quantity, the salt was recrystallised from a dilute solution, and again allowed to dry in the air.

0.3016, on drying at 100° , lost 0.0436 H_2O . $\text{H}_2\text{O} = 14.5$.

The air-dried and the dehydrated salts were then analysed :

0.2021 of air-dried salt gave 0.3860 CO_2 and 0.1270 H_2O .
 C = 52.1 ; H = 7.0.

0.2048 of salt, dried at 100°, gave 0.4591 CO₂ and 0.1143 H₂O.

C = 61.1; H = 6.2.

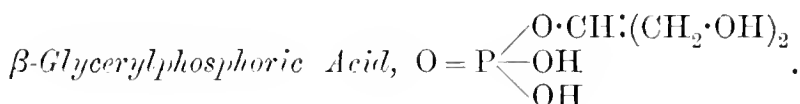
C₄₉H₆₁O₁₄N₄P, 9H₂O requires C = 52.4; H = 6.9; H₂O = 14.4 per cent.

C₄₉H₆₁O₁₄N₄P requires C = 61.3; H = 6.3 per cent.*

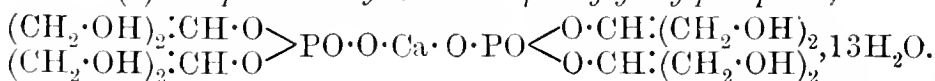
The specific rotation of the salt dried at 100° was determined in aqueous and in alcoholic solution.

0.2178, dissolved in 25 c.c. of absolute alcohol, gave α_D - 34' in a 2-dcm. tube, whence [α]_D - 32.5°.

0.1608, dissolved in 25 c.c. of water, gave α_D - 19.5' in a 2-dcm. tube, whence [α]_D - 25.3°.



(a) Preparation of Calcium β-Diglycerolphosphate,



The α-dichlorohydrin required for this preparation was obtained from Kahlbaum, and was submitted to a careful fractionation. Only the portion boiling from 173—176° was employed, which was found to be pure. Equivalent molecular proportions of α-dichlorohydrin and phosphoryl chloride were boiled together in a round-bottomed flask attached to a reflux condenser, when a copious evolution of hydrogen chloride ensued. At the end of two and three-quarter hours the dark liquid was poured into a large excess of milk of lime, the mixture boiled for two hours in a flask attached to a reflux condenser, then filtered, and the excess of lime removed from the filtrate by means of carbon dioxide. On evaporating the filtrate, the crude calcium β-diglycerolphosphate, which separated as a scum on the surface of the liquid, was removed from time to time and dried on a porous tile. From 50 grams of the dichlorohydrin about 18 grams of crude calcium salt were obtained. When crystallised from water, *calcium β-diglycerolphosphate* was obtained in long, slender needles, which melted at 249—250°. It dissolves very readily in alcohol and in ethyl acetate, but less readily in water, chloroform, or benzene; it is insoluble in light petroleum. When the crystallised salt is heated, it suffers a decrease in weight, but it was found impracticable to estimate the water of crystallisation by this method, as the temperature necessary for complete dehydration also causes gradual decomposition.

0.3081 of air-dried salt gave 0.0230 CaO. Ca = 5.3.

The air-dried salt was then analysed in the usual manner.

* One atom of hydrogen becomes fixed as HPO₃.

0.1804 gave 0.1243 CO_2 ; 0.1169 H_2O , and 0.466 of residue, $\text{Ca}(\text{PO}_3)_2$.

$\text{C} = 18.8$; $\text{H} = 7.2$; $\text{Ca}(\text{PO}_3)_2 = 25.8$.

$\text{C}_{12}\text{H}_{28}\text{O}_{16}\text{P}_2\text{Ca}, 13\text{H}_2\text{O}$ requires $\text{C} = 18.8$; $\text{H} = 7.1$; $\text{Ca} = 5.2$; $\text{Ca}(\text{PO}_3)_2 = 25.9$ per cent.

(b) *Hydrolysis of β -Diglycerolphosphoric Acid*.—Calcium β -diglycerolphosphate was dissolved in water, two-thirds of the amount of sulphuric acid theoretically required to combine with the calcium added, and the mixture boiled for four hours. Excess of calcium hydroxide was then introduced, the mixture cooled, filtered, and the filtrate freed from the excess of lime by means of carbon dioxide. The filtrate was then evaporated to a small bulk, and the calcium β -glycerolphosphate, together with the calcium sulphate, precipitated by the addition of alcohol, and collected on a filter. The alcoholic filtrate contained some unchanged calcium β -diglycerolphosphate, from which a further quantity of the β -glycerolphosphate was obtained.

Barium β -Glycerolphosphate, $\text{O} = \text{P} \begin{array}{l} \text{O} \cdot \text{CH} : (\text{CH}_2 \cdot \text{OH})_2 \\ \text{O} \end{array} \text{Ba}$.—The crude

mixture of calcium β -glycerolphosphate and calcium sulphate was converted into the barium salts, and the barium sulphate removed by filtration. On evaporating the filtrate, barium β -glycerolphosphate separated as a white, amorphous powder, and was removed by filtration. It was then redissolved in cold water, the solution concentrated on a water-bath, and the barium salt which separated was collected on a filter. This operation was repeated several times, but the salt showed no indication of possessing a crystalline structure. From 45 grams of crude calcium β -diglycerolphosphate about 3 grams of barium β -glycerolphosphate were obtained.

0.5108 of air-dried salt, on heating at 125° , lost 0.0259 H_2O .
 $\text{H}_2\text{O} = 5.1$.

$\text{C}_3\text{H}_7\text{O}_6\text{PBa}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 5.5$ per cent.

0.4849 dried at 125° , gave 0.3643 BaSO_4 . $\text{Ba} = 44.2$.

$\text{C}_3\text{H}_7\text{O}_6\text{PBa}$ requires $\text{Ba} = 44.6$ per cent.

9.9378 of an aqueous solution, saturated at 17° , gave on evaporation 0.2702 of residue, therefore one part of the salt is contained in 36.8 parts of solution.

Brucine β -Glycerolphosphate, $\text{O} = \text{P} \begin{array}{l} \text{O} \cdot \text{CH} : (\text{CH}_2 \cdot \text{OH})_2 \\ \text{OH}, \text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \\ \text{OH}, \text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2 \end{array}$, $11\frac{1}{2} \text{H}_2\text{O}$.—

This salt, prepared in the manner previously described, crystallises from water in stout needles, and, after drying at 100° , melted at 157 — 158° .

0.4283, on drying at 100° , lost 0.0759 H_2O . $\text{H}_2\text{O} = 17.7$.

0.1981 of air-dried salt gave 0.3652 CO_2 and 0.1324 H_2O . $\text{C} = 50.3$;
 $\text{H} = 7.4$.

0.1893 of air-dried salt gave 0.3484 CO_2 and 0.1256 H_2O . $\text{C} = 50.2$;
 $\text{H} = 7.4$.

0.1787, dried at 100° , gave 0.4007 CO_2 and 0.1052 H_2O . $\text{C} = 61.2$;
 $\text{H} = 6.5$.

$\text{C}_{49}\text{H}_{61}\text{O}_{11}\text{N}_4\text{P}$, $11\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 50.4$; $\text{H} = 7.1$; $\text{H}_2\text{O} = 17.7$
 per cent.

$\text{C}_{49}\text{H}_{61}\text{O}_{14}\text{N}_4\text{P}$ requires $\text{C} = 61.3$; $\text{H} = 6.3$ per cent.

0.2071, dissolved in 25 c.c. of absolute alcohol, gave $\alpha_D - 28'$ in a
 2-dem. tube, whence $[\alpha]_D - 28.1^\circ$.

0.1600, dissolved in 25 c.c. of water, gave $\alpha_D - 18.4'$ in a 2-dem.
 tube, whence $[\alpha]_D - 23.9^\circ$.

Natural Glycerolphosphoric Acid.

The lecithin from which the racemised natural glycerolphosphoric acid was prepared was obtained in the form of its cadmium chloride compound according to Bergell's method (*loc. cit.*), and for this purpose the yolks of 144 eggs were employed. This cadmium chloride compound was purified by recrystallisation from a mixture of ethyl acetate and alcohol (compare Willstätter and Lüdecke, *loc. cit.*).

Barium Salt of Natural Glycerolphosphoric Acid.—The purified cadmium chloride compound of lecithin was boiled for one hour with a solution of barium hydroxide, the mixture then cooled, filtered, and the filtrate deprived of the excess of baryta by means of carbon dioxide. On concentrating the clear liquid, the barium salt of the natural glycerolphosphoric acid was deposited in the form of caseous flakes. This salt was optically inactive, having been racemised by the use of boiling liquids (Willstätter and Lüdecke, *loc. cit.*). It was recrystallised from water, when it was obtained in nodular aggregates of leaflets.

0.3950 of air-dried salt, on heating at 125° , lost 0.0093 H_2O .
 $\text{H}_2\text{O} = 2.4$.

$\text{C}_3\text{H}_7\text{O}_6\text{P}\text{Ba}$, $\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 2.8$ per cent.

0.3857, dried at 125° , gave 0.2912 BaSO_4 . $\text{Ba} = 44.4$.

$\text{C}_3\text{H}_7\text{O}_6\text{P}\text{Ba}$ requires $\text{Ba} = 44.6$ per cent.

5.5110 of an aqueous solution, saturated at 17° , gave on evaporation 0.3968 of residue, therefore one part of the salt is contained in 13.9 parts of solution.

Brucine Salt of Natural Glycerolphosphoric Acid.—This salt was prepared in the same manner as the previously described brucine salts.

When crystallised from water, it was obtained in stout needles, which, after drying at 100° , melted at $158-159^{\circ}$.

0.4972, on drying at 100° , lost $0.0526 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 10.6$.

The estimation of the water of crystallisation was then repeated, using another sample of salt.

0.2980, on drying at 100° , lost $0.0314 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 10.5$.

The air-dried and the anhydrous salt were subsequently analysed, with the following results :

0.1946 of air-dried salt gave 0.3876 CO_2 and $0.1240 \text{ H}_2\text{O}$. $\text{C} = 51.3$; $\text{H} = 7.1$.

0.2332 of salt dried at 100° gave 0.5196 CO_2 and $0.1356 \text{ H}_2\text{O}$. $\text{C} = 60.8$; $\text{H} = 6.5$.

$\text{C}_{49}\text{H}_{61}\text{O}_{11}\text{N}_4\text{P}, 6\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 54.6$; $\text{H} = 6.8$; $\text{H}_2\text{O} = 10.9$ per cent.

$\text{C}_{49}\text{H}_{61}\text{O}_{11}\text{N}_4\text{P}$ requires $\text{C} = 61.3$; $\text{H} = 6.3$ per cent.

0.2464, dissolved in 25 c.c. of absolute alcohol, gave $\alpha_D = -33'$ in a 2-dem. tube, whence $[\alpha]_D = -27.9^{\circ}$.

0.1593, dissolved in 25 c.c. of water, gave $\alpha_D = -18.3'$ in a 2-dem. tube, whence $[\alpha]_D = -23.9^{\circ}$.

Synthetical Glycerolphosphoric Acid.

The barium salt of the synthetical glycerylphosphoric acid was prepared under such conditions as are known to yield only the mono-ester (compare Carré, *Compt. rend.*, 1903, 137, 1070 ; Power and Tutin, *Trans.*, 1905, 87, 249). It was recrystallised from water, when it was obtained as a granular powder.

0.3036 of air-dried salt, on heating at 125° , lost $0.0077 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 2.5$.

$\text{C}_3\text{H}_7\text{O}_6\text{P}\text{Ba}, \frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 2.8$ per cent.

5.9158 of an aqueous solution, saturated at 17° , gave on evaporation 0.1102 of residue, therefore one part of the salt is contained in 53.7 parts of solution.

Brucine Salt of Synthetical Glycerolphosphoric Acid.—This salt was prepared in the same manner as the previously described brucine salts, and possessed the same appearance and melting point as the brucine salt of the natural acid.

0.4987, on drying at 100° , lost $0.0570 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 11.4$.

0.4948, „ „ 100° , „ $0.0588 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 11.9$.

0.3750, „ „ 100° , „ $0.0448 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 11.9$.

0.2064 of air-dried salt gave 0.4070 CO_2 and 0.1324 H_2O . $\text{C} = 53.8$;
 $\text{H} = 7.0$.

0.1968, dried at 100° , gave 0.4392 CO_2 and 0.1156 H_2O . $\text{C} = 60.9$;
 $\text{H} = 6.5$.

$\text{C}_{49}\text{H}_{61}\text{O}_{14}\text{N}_4\text{P}, 7\text{H}_2\text{O}$ requires $\text{C} = 54.1$; $\text{H} = 6.8$; $\text{H}_2\text{O} = 11.6$ per cent.

$\text{C}_{49}\text{H}_{61}\text{O}_{14}\text{N}_4\text{P}$ requires $\text{C} = 61.3$; $\text{H} = 6.3$ per cent.

0.2366, dissolved in 25 c.c. of absolute alcohol, gave $\alpha_D - 32'$ in a 2-dm. tube, whence $[\alpha]_D - 28.2^\circ$.

0.1607, dissolved in 25 c.c. of water, gave $\alpha_D - 19'$ in a 2-dm. tube, whence $[\alpha]_D - 24.6^\circ$.

The brucine salt of the synthetical glycerylphosphoric acid was also prepared by Carré (*loc. cit.*), who assigned to it a formula containing 9 molecules of water, whereas the above results indicate the presence of only 7 molecules. In addition to this, Carré stated the melting point of the salt to be 181° , whereas it has been observed by the present authors to be $158-159^\circ$. It was considered possible that these discrepancies were due to the fact that Carré prepared his brucine salt from the free acid, while the brucine salts described in the present communication were all prepared from the corresponding barium salts by double decomposition. In other words, as the synthetical glycerylphosphoric acid appears to be a mixture, and undergoes slow hydrolysis when heated with water, it was thought possible that the free acid used by Carré might have become altered in composition on account of its constituents differing in their relative velocities of hydrolysis. The acid was therefore liberated from a quantity of the synthetical barium salt, and boiled with water for two and a half hours. It was then converted into the brucine salt, and the latter crystallised, when it was found to be identical with the preceding preparation.

0.3032, when heated at 100° , lost 0.0354 H_2O . $\text{H}_2\text{O} = 11.7$.

$\text{C}_{49}\text{H}_{61}\text{O}_{14}\text{N}_4\text{P}, 7\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.6$ per cent.

The melting point of the dried salt was the same as previously observed. The authors are therefore unable to confirm the figures given by Carré for the melting point and water of crystallisation of the brucine salt of synthetical glycerylphosphoric acid.

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CLXXI.—*The Hydrolysis of "Nitrocellulose" and "Nitroglycerine."*

By OSWALD SILBERRAD, Ph.D., and ROBERT CROSBIE FARMER,
D.Sc., Ph.D.

WE have recently shown (*J. Soc. Chem. Ind.*, 1906, 25, 961) that the gradual decomposition of nitrocellulose which takes place on storage, is largely hydrolytic in nature, being brought about by the moisture of the air, under the influence of traces of acid liberated from the nitric esters. With the object of gaining a closer insight into the mechanism of the decomposition of nitrocellulose, nitroglycerine, and mixtures of the two, the hydrolysis of these esters has been more fully studied in the present work.

Abnormality of the Hydrolysis of Nitric Esters.—The subject is somewhat complicated by the abnormality of the reactions which occur during the hydrolysis. It has been shown by Ador and Sauer (*Zeit. anal. Chem.*, 1878, 17, 153), Hay (*Monit. Scient.*, 1885, [iii], 27, 424; *Trans. Roy. Soc. Edin.*, 1885, 32, 67); Maquenne (*Ann. Chim. Phys.*, 1891, [vi], 24, 522); Berthelot (*Ann. Chim. Phys.*, 1860 [iii], 58, 447; *Compt. rend.*, 1900, 131, 519); Nef (*Annalen*, 1899, 309, 181), and Vignon and Bay (*Compt. rend.*, 1902, 135, 507; *Bull. Soc. Chim.*, 1903, [iii], 29, 507), that the saponification of nitric esters is always accompanied by a reduction of the nitric acid and a corresponding oxidation of the alcohol. The authors have shown (*Trans.*, 1906, 89, 1182) that in the case of nitrocellulose the product is a highly complex mixture of hydroxy-acids, &c.

This abnormality of the hydrolysis has been confirmed in several ways in the present work.

(1) When nitrocellulose is hydrolysed in alkaline solution, nitrites are formed in considerable quantity and various organic salts pass into solution.

(2) Saponification equivalent: It is found that both nitrocellulose and nitroglycerine neutralise much more alkali than can be accounted for by the nitroxyl groups present. Thus a nitrocellulose containing 5.04 nitroxyl groups neutralised 9.2 to 9.5 equivalents of baryta. If the nitroxyl groups only had entered into reaction, the nitrocellulose would have required only 5.04 equivalents of baryta, and thus the remainder must have been used in neutralising acids formed by the breaking down of the cellulose.

Similarly, nitroglycerine, which should require only 3 equivalents of alkali, gave a saponification equivalent corresponding to 4.85 equivalents.

According to Hay (*Monit. Scient.*, 1873, [iii], 15, 507 ; 1885, [iii], 27, 424), the saponification of nitroglycerine takes place mainly in accordance with the following equation :



One gram-molecule of nitroglycerine would thus require 5 gram-equivalents of caustic potash, which agrees moderately well with the result found. The reaction is, however, certainly not so simple as indicated by Hay.

(3) Velocity of saponification: Instead of showing the normal decrease in velocity which would be expected to occur as the quantities of the reagents decreased, the saponification continued to take place at approximately the same velocity until a large proportion of the alkali was used up. This proves that products other than nitrocellulose entered into the reaction. The saponification of the nitrocellulose must give rise to intermediate products which are also gradually acted on by alkali, and thus the saponification measured during the latter stages of the reaction is not that of the nitrocellulose alone, but is in part a hydrolysis of decomposition products of cellulose.

These intermediate products are insoluble in water, for it was found that when the alkaline liquid was separated from the nitrocellulose, the saponification ceased almost entirely in the filtrate.

Nitroglycerine, being much more readily soluble in water than nitrocellulose, undergoes a correspondingly more rapid saponification in alkaline solution. The course of the reaction shows an abnormality similar to that found in the case of nitrocellulose.

It is somewhat surprising that no unchanged cellulose or glycerol should be regenerated on hydrolysis, for if nitric acid is brought into contact with cellulose or glycerol in the concentrations which come into consideration in the hydrolysis, no oxidation occurs. It appears that the nitric acid which has just been set free from the nitric ester is in a more active condition than nitric acid in its ordinary form.

Hydrolysis of nitrocellulose in pure water.—Since nitrocellulose is gradually hydrolysed both by hydrogen- and hydroxyl-ions, it follows that a slight hydrolysis will occur even in pure water, owing to the minute dissociation of the water. It is to be foreseen that, on passing from alkaline to acid solution, the velocity of hydrolysis will decrease to a minimum and then gradually increase again. Thus, although it is frequently assumed that absolutely pure water is without action on nitrocellulose, this assumption is not strictly correct. Hydroxyl ions are much more active than hydrogen ions, and hence the minimum velocity occurs in presence of a slight excess of hydrogen ions. The

concentrations of hydrogen- and hydroxyl-ions necessary to produce the minimum velocity of hydrolysis can be calculated from the velocities of saponification in acid and alkaline solution respectively. It must, however, be taken into account that in the comparatively rapid hydrolysis which takes place in presence of acid or alkali of moderate strength, the diffusion of the nitrocellulose into the aqueous solution is imperfect, whilst in the slow decomposition which occurs in presence of water alone the solution remains saturated with nitrocellulose throughout the reaction. This has been allowed for in the calculations, and it is found that at 37.8° the hydrolysis will take place with its minimum velocity, when the concentration of the hydrogen ions is 3.7×10^{-6} and that of the hydroxyl ions 7.8×10^{-9} . Under these conditions, the gun-cotton will liberate 5.6×10^{-5} gram-equivalents of acid per litre of water per year. In practice the decomposition is of course accelerated by the acid set free.

It should be pointed out that a solution containing 3.7×10^{-6} gram-equivalents of hydrogen ions per litre reacts appreciably acid to sensitive litmus. Hence it appears that if gun-cotton is allowed to remain in water, no acceleration takes place in the hydrolysis as long as the solution is neutral to litmus. It is seen from this that storage under water forms the safest method of keeping gun-cotton, since under these conditions the impurities will decompose without any appreciable effect on the nitrocellulose itself. In this way nitrocellulose of a remarkable degree of stability has at times been obtained (compare Hess, *Mitt. über Gegenst. d. Art. und Geniewesens*, 1881, 240; Romocki, *Geschichte d. Explosivstoffe*, II., 154, &c.).

Hydrolysis of gelatinised nitrocellulose, &c.—Gelatinised nitrocellulose differs so strongly from gun cotton in the compactness of its structure, that it appeared of importance to ascertain whether it underwent a similar hydrolysis in presence of alkali. The course of the reaction was found to be quite analogous in the two forms of nitrocellulose.

In view of the wide application of gelatinised preparations, containing both nitrocellulose and nitroglycerine, an examination of their hydrolysis was of practical importance. Their behaviour is somewhat interesting. It is known that nitroglycerine volatilises fairly readily from explosives containing it, and since experiment shows that this ester saponifies rapidly in alkaline solution, it is to be expected that the nitroglycerine from such explosives will also undergo a similar hydrolysis. This is confirmed by experiments on corditè and ballistite. Both of these show a rapid hydrolysis in alkaline solution. An analysis of the residual cordite after hydrolysis shows that the hydrolysis is due almost entirely to nitroglycerine which has passed from the explosive into the aqueous solution. Thus it was found that

70 per cent. of the nitroglycerine in a cordite had undergone saponification, whilst the nitrocellulose was almost unaltered.

This throws considerable light on the mechanism of the changes which occur when cordites are subjected to prolonged storage, and the relative stability of cordite as compared with nitrocellulose powders when stored in a damp atmosphere.

EXPERIMENTAL.

Saponification equivalent of nitrocellulose.—For the following experiments a gun-cotton corresponding approximately to cellulose pentanitrate was used. The percentage of nitrogen was 12·84, and thus, if cellulose is considered as $(C_{12}H_{20}O_{10})_x$, the nitrocellulose contained $5.04 x$ nitroxyl groups, and had a molecular weight of $550.2 x$.

For the determination of the saponification equivalent, a weighed quantity of the gun-cotton was allowed to stand, with occasional shaking, in presence of excess of baryta, at 39°, and after several days a portion of the baryta was titrated. On allowing the remainder to stand for another day, no difference in the titration was detected. An insoluble residue remained in the vessel after completion of the saponification, but this gave no nitric oxide in the nitrometer. The liquid proved to contain large quantities of barium nitrite.

In the first experiment, a large excess of baryta was taken, and in the second a comparatively small excess. The saponification equivalent found was almost identical in the two experiments, showing that the reaction is not affected by the excess of alkali.

	(i).	(ii).
Grams of nitrocellulose used.....	1.68	2.98
Gram-equivalents of baryta present for each gram-mol. of nitrocellulose	37.8	14.8
Gram-equivalents of baryta neutralised by 1 gram-mol. of nitrocellulose	9.5	9.2

Thus the saponification equivalent is 85 per cent. in excess of that calculated for a nitric ester of the above composition.

Saponification equivalent of nitroglycerine.—Nitroglycerine is so sparingly soluble in water that it could not be brought completely into solution before the experiments. Even the addition of an equal volume of methyl or ethyl alcohol to the water did not bring about any great increase in the solubility. The saponification takes place, however, with considerable rapidity in presence of alkali. For the determination of the saponification equivalent, a weighed quantity was treated with excess of baryta as above. If only the nitroxyl groups entered into the reaction, each gram-molecule of nitroglycerine would

require 3 gram-equivalents of baryta. In practice it was found that 4.85 gram-equivalents were required.

Grams of nitroglycerine used	0.3085
Gram-equivalents of baryta present for each gram-mol. of nitro-glycerine	5.17
Gram-equivalents of baryta neutralised by 1 gram-mol. of nitro-glycerine	4.85

Experiments by Silberrad, Phillips and Merriman (*J. Soc. Chem. Ind.*, 1906, 25, 628), in which an ethereal solution of nitroglycerine was saponified by alcoholic caustic alkali, gave 4.23 to 4.45 equivalents of alkali for each molecule of nitroglycerine. Since, however, nitroglycerine is readily volatile in ether vapour, it is probable that some loss of ester occurred in this way.

Velocity of Saponification of Gun-cotton by Hydroxyl Ions.—A weighed quantity of a gun-cotton containing 12.5 per cent. of nitrogen, corresponding to 4.82 nitroxyl groups, was suspended in a solution of baryta and stirred continuously. The temperature was retained at $37.8 \pm 0.1^\circ$ (100° F.), this being about the limit of temperature to which explosives are liable to be exposed on storage. At intervals the gun-cotton was allowed to settle, and quantities of 10 c.c. of the solution were withdrawn by a pipette through a small piece of cloth, which excluded any fibres of gun-cotton. The liquid was titrated, phenolphthalein being used as indicator. The solution was protected, as far as possible, from the air throughout the experiment, and a blank test showed that the influence of the carbon dioxide of the air was negligible.

Hydrolysis of Gun-cotton by Baryta Solution.

Percentage of nitrogen in gun-cotton = 12.5. Temperature = 37.8° . Initial volume of baryta solution = 400 c.c. Quantity taken for each titration = 10 c.c.

1. Quantity of gun-cotton = 22.10 grams.

Time in hours.	C.c. of 0.201-normal acid required.	Concentration of baryta (gram-equiv. per litre).
0.0	9.40	0.189
1.5	8.30	0.167
4.5	6.25	0.126
5.0	5.85	0.118
5.5	5.65	0.114
6.0	5.30	0.107
6.5	4.95	0.100
7.0	4.55	0.091
7.5	4.10	0.082
23.0	0.15	0.003

Initial velocity = 0.0142 gram-equivalent per hour.

2. Quantity of gun-cotton = 20.42 grams.

Time in hours.	C.c. of 0.201-normal acid required.	Concentration of baryta (gram-equiv. per litre.)
0.0	4.80	0.096
0.5	4.55	0.091
1.0	4.35	0.087
2.0	4.00	0.080
2.5	3.90	0.078
3.5	3.50	0.070
5.0	2.90	0.058
6.0	2.60	0.052
7.0	2.30	0.046

Initial velocity = 0.0071 gram-equivalent per hour.

3. Quantity of gun-cotton = 4.97 grams.

0.0	9.5	0.191
0.5	9.3	0.187
1.0	9.2	0.185
2.0	9.1	0.183
2.5	9.0	0.181
4.0	8.6	0.172
5.0	8.25	0.166
6.0	7.95	0.160
7.0	7.65	0.154
23.0	3.15	0.063
24.0	2.90	0.058
25.0	2.70	0.054
26.0	2.45	0.049
29.0	2.05	0.041
30.0	1.85	0.037
31.0	1.70	0.034

Initial velocity = 0.0053 gram-equivalent per hour.

4. Quantity of gun-cotton = 3.10 grams.

0.0	9.8	0.197
1.0	9.65	0.194
1.5	9.40	0.189
3.0	9.20	0.185
4.5	9.00	0.181
6.0	8.80	0.177
22.0	5.25	0.105
25.0	4.60	0.092
30.0	3.9	0.078
46.0	2.45	0.049

Initial velocity = 0.0033 gram-equivalent per hour.

These results are shown graphically in Fig. 1, and it is seen that the curves are almost straight, showing that the velocity is almost constant until the bulk of the gun-cotton is used up.

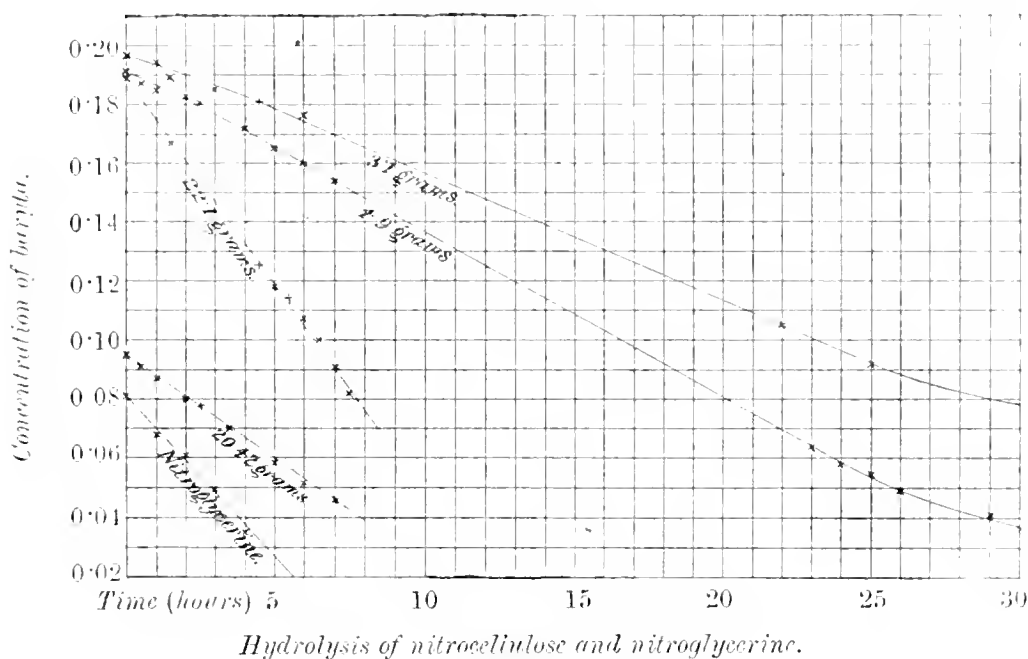
A comparison of the first two experiments given above shows that the velocity of saponification is almost proportional to the original concentration of the baryta. No such simple relationship exists

between the amount of gun-cotton present and the velocity. If diffusion took place sufficiently rapidly to keep the solution saturated with respect to the gun-cotton, the active mass of the nitrocellulose could be considered as constant, and the velocity would not be affected by the quantity of gun cotton present.

This holds good approximately (though not absolutely) in the experiments given later in which hydrolysis of gun-cotton by nitric acid was measured, since the reaction in this case is extremely slow. In the above experiments, however, the hydrolysis occurs so rapidly that the solution can never be regarded as fully saturated with nitrocellulose, and hence the amount of surface exposed becomes an important factor.

If the amount of surface of the gun-cotton were the only factor

FIG. 1.



which determined its active mass, we should expect the velocity to be proportional to the quantity of gun-cotton. This also does not hold absolutely; the velocities show that the active mass of the gun-cotton is neither a constant, nor is it proportional to the quantity added, but lies somewhere between the two, its value depending on the rate with which the nitrocellulose passes into solution, and the degree of saturation which is thereby maintained. If we consider the saponification of varying amounts of gun-cotton in a normal solution of alkali, an equilibrium is obviously reached when the rate at which the nitrocellulose passes into solution is equal to the rate at which it undergoes saponification. If we consider the water as partially saturated with free nitrocellulose, we may assume that the rate at which solid nitro-

cellulose is passing into solution at any moment is proportional (1) to the amount of surface exposed, that is, to the quantity of gun-cotton present, (2) to the difference between the amount of gun-cotton present in solution and the amount necessary to saturate the aqueous solution. This is, in its turn, proportional to the difference between the observed velocity and the limiting velocity which would result if the solution were kept saturated with respect to the gun-cotton—that is, supposing that the saponification commences with the elimination of one of the nitroxyl groups. Thus the relation between the velocity and the quantities of the reagents may be expressed by the equation $q(s - v) = kv$, where q = weight of gun-cotton (grams per 400 c.c.), v = observed velocity, s = limiting velocity for a solution saturated with gun-cotton, and k = a constant. Further, since the velocity is proportional to the concentration of the baryta, we may write

$$v = \frac{cqs}{k + q}, \text{ } c \text{ being the concentration of the baryta.}$$

From the above data we find that under the present conditions $s = 0.168$, $k = 26.5$. From these we calculate the following velocities, which agree closely with those found by experiment.

Saponification of Nitrocellulose by Baryta at 37° 8°.

Grams of gun-cotton.	Concentration of baryta.	Velocity (gram-equiv. per hour).	
		$V = cqs/k + q.$	Found.
3.10	0.197	0.0035	0.0033
4.97	0.191	0.0051	0.0053
20.42	0.096	0.0070	0.0071
22.10	0.189	0.0144	0.0142
0.00	1.000	0.168	—

The chief value of this formula is that it enables us to calculate the velocity with which the saponification would occur if the solution remained continuously saturated with respect to the gun-cotton. In a normal solution this becomes equal to s . This is of importance, because it corresponds most closely to the conditions under which the slow hydrolysis occurs in practice.

Abnormality in the course of the Saponification.—In the curves showing the decrease in the concentration of the baryta during the saponification, the velocity is seen to be approximately constant. It must not, however, be overlooked that, as the liquid is withdrawn from time to time with the pipette, the “concentration” of the gun-cotton in the remaining liquid increases. With the help of the relation between the quantities of the reagents and the velocity, found above, it is possible to ascertain whether the saponification takes place normally throughout. The first of the above series will serve as an example. The con-

centration of baryta after each interval is given as before. The quantity of gun-cotton is given in “grams per 400 c.c.” to allow for the increase in concentration.

Time in hours.	Concen- tration of baryta.	Volume of solution in c.c.	Grams of gun-cotton per 400 c.c. of solution.	Velocity calculated from con- centrations.	Velocity found.
0·0	0·189	400	22·1	0·0144	0·0147
1·5	0·167	390	22·1	0·0128	0·0147
4·5	0·126	380	21·7	0·0095	0·0140
5·0	0·118	370	22·2	0·0090	0·0142
5·5	0·114	360	22·6	0·0088	0·0137
6·0	0·107	350	23·1	0·0084	0·0137
6·5	0·100	340	23·6	0·0079	0·0137
7·0	0·091	330	24·1	0·0073	0·0149
7·5	0·082	320	24·6	0·0066	0·0143

The velocity is thus seen to be normal at first, but does not decrease, as would be expected from mass action considerations, showing that, as the reaction proceeds, intermediate products are formed which are also acted on by the baryta. The remaining series of results gives precisely similar indications.

Insolubility of the Intermediate Products.—A gun-cotton containing 12·84 per cent. of nitrogen (corresponding approximately to penta-nitrate) was suspended in a baryta solution as above, and retained at 39° with constant agitation until a considerable amount of saponifica-tion had occurred. The solution was then rapidly filtered and the filtrate replaced in the thermostat; the titrations were continued at intervals, but only a very slight decrease in the alkalinity was observed, this being probably due to traces of finely divided gun-cotton which passed through the filter paper.

Time in hours.	Volume of solution.	C.c. of 0·2027 normal acid required for 10 c.c. of solution.	Concentration of baryta (gram- equiv. per litre).
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10 grams gun-cotton. 400 c.c. baryta solution. Temp. = 39°.

0	400	9·85	0·200
1	390	9·60	0·195
2	380	9·25	0·188
4	370	9·05	0·183
23½	340	3·60	0·073

Filtered off solid gun-cotton, and replaced filtrate in thermostat.

24½	328	3·45	0·070
26	318	3·35	0·068
30	308	3·30	0·067
48½	298	3·25	0·066

Further experiments were carried out, in which a solution of baryta was treated with excess of nitrocellulose, and the reaction allowed to proceed for a considerable time, to ascertain whether the intermediate products of the saponification would continue to decompose after the

baryta was exhausted. No acidity set in, however, even after twelve days at 39°.

Velocity of Hydrolysis of Gun-cotton by Hydrogen Ions.

The hydrolysis is so much slower in acid than in alkaline solution that it was found necessary to enclose the acid and gun-cotton in stoppered bottles to avoid evaporation. The bottles were enclosed in a thermostat and agitated frequently. From time to time quantities of 10 c.c. were withdrawn and titrated with baryta.

Hydrolysis of Gun-cotton by Nitric Acid.

Percentage of nitrogen in gun-cotton = 12.5, temperature = 37.8°.

1. Quantity of gun-cotton = 5.1 grams.

Time in hours.	C.c. of 0.2139 normal alkali for 10 c.c. of liquid.	Concentration of nitric acid (gram-equiv. per litre).
0	38.40	0.821
22	38.50	0.824
45	38.85	0.831
70	38.90	0.832
94	39.05	0.835
144	39.45	0.844
168	39.75	0.850
192	40.10	0.858
240	40.55	0.867

Initial velocity = 0.000175 gram-equivalent per hour.

2. Quantity of gun-cotton = 10 grams.

0	38.40	0.821
22	38.60	0.826
45	38.90	0.832
70	39.00	0.834
94	39.25	0.840
144	39.75	0.850
168	40.05	0.857
192	40.55	0.867
240	40.85	0.874

Initial velocity = 0.000221 gram-equivalent per hour.

3. Quantity of gun-cotton = 20.35 grams.

0	38.40	0.821
22	38.80	0.830
45	39.05	0.835
70	39.20	0.838
94	39.55	0.846
144	39.95	0.855
168	40.15	0.859
192	40.70	0.871
240	41.10	0.879

Initial velocity = 0.000212 gram-equivalent per hour.

The velocities are constant within the limits of experimental error. If the relation between the velocity of reaction and the concentrations of the reagents be expressed as before by the formula $V = \frac{cqs}{k+q}$, we find $s = 0.000347$; $k = 3.21$.

Grams of gun-cotton.	Concentration of nitric acid.	Velocity (gram-equiv. per hour).	
		$V = cqs/k + q$.	Found.
5.10	0.821	0.00018	0.00018
10.00	0.821	0.00022	0.00021
20.35	0.821	0.00025	0.00024
0.00	1.000	0.000347	—

The gun-cotton was decomposed so slowly that the aqueous solution remained almost saturated.

Hydrolysis of Nitrocellulose in Pure Water.—From the above data the velocity of hydrolysis of nitrocellulose in pure water can be calculated. This velocity is so low that it must be assumed that perfect diffusion takes place—that is, the water remains saturated with gun-cotton. With the aid of the above formulæ it was found possible to calculate the velocity of hydrolysis by hydrogen- and hydroxyl-ions respectively, allowing for perfect diffusion of the nitrocellulose. In this way the following velocities are obtained:

	Velocity in gram-equivalents per litre per hour.
In a normal solution of hydrogen ions.....	0.00037
„ „ hydroxyl „	0.420

The dissociation of pure water has been determined with considerable accuracy by Ostwald, Arrhenius, Wijs, Nernst, Kohlrausch and Heydweiller, Löwenherz, and Walker (*Zeit. physikal. Chem.*, 1893, 11, 521, 827; 12, 514; 1894, 14, 155, 317; 1896, 20, 283; 1900, 32, 137). At 37.8° , the temperature of the above experiments, the product of the concentrations of the hydrogen- and hydroxyl-ions may be taken as 2.9×10^{-14} .

It is seen that the hydrolysis of nitrocellulose takes place 480 times as rapidly in alkali as in acid of the same concentration; hence the minimum velocity will be attained when the concentration of the hydrogen ions is 480 times that of the hydroxyl ions.

The absolute concentrations will then be

$$\text{H-ions: } \sqrt{480} \times 1.7 \times 10^{-7} = 3.7 \times 10^{-6}.$$

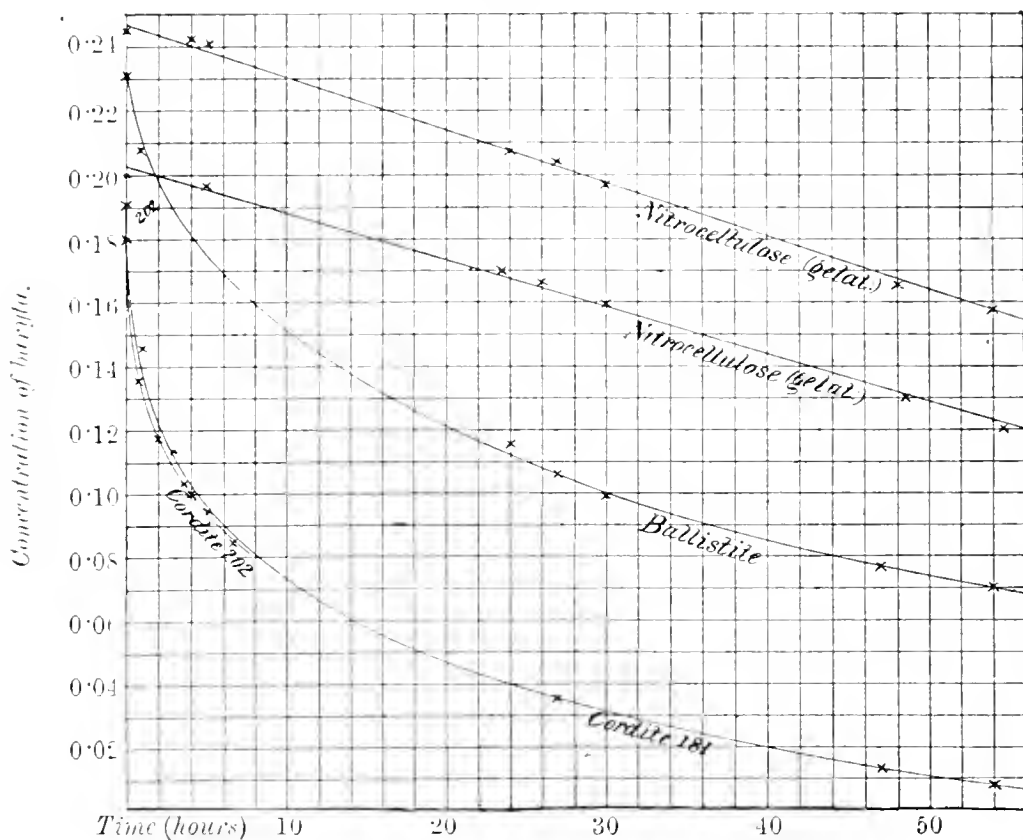
$$\text{OH-ions: } \sqrt{\frac{1}{480}} \times 1.7 \times 10^{-7} = 7.8 \times 10^{-9}.$$

Under these conditions the velocity due to the hydrogen ions will be 3.2×10^{-9} , and the combined velocity will therefore be 6.4×10^{-9}

gram-equivalents per litre per hour. In other words, the minimum velocity with which a nitrocellulose of the above composition can undergo hydrolysis will be such as to liberate 5.6×10^{-5} gram-equivalents of acid per litre of water per year.

Hydrolysis of Gelatinised Nitrocellulose.—In order to ascertain whether gelatinised nitrocellulose still undergoes a similar hydrolysis,

FIG. 2.



Hydrolysis of gelatinised powders.

a sample was finely ground and suspended in baryta water. The saponification took place in very much the same way as in the case of gun-cotton, as shown by the following instance:

Nitrocellulose gelatinised with ether-alcohol.

Analysis: Soluble in ether-alcohol.....	85.58
Insoluble „	10.18
Insoluble in acetone	0.42
Volatile matter	3.82
Nitrogen	11.85

Ground to pass through a sieve of 0.85 mm. mesh.

Quantity of nitrocellulose = 10.00 grams.

Time in hours.	Volume of solution.	C.c. of 0.2027 normal acid required.	Concentration of baryta (gram- equiv. per litre).
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(i). In 0.200 normal baryta :

0	400	9.85	0.200
5	360	9.70	0.197
6	350	9.60	0.195
23.5	310	8.40	0.170
26	330	8.25	0.167
30	320	7.85	0.159
48.5	310	6.45	0.130
54.5	300	5.90	0.120
72	290	4.80	0.097
119.5	280	2.25	0.046

Mean velocity = 0.00143 gram-equivalent per hour.

(ii). In 0.246 normal baryta :

0	400	12.15	0.246
4	370	12.00	0.243
5	360	11.90	0.241
24	350	10.35	0.210
27	340	10.05	0.204
30	330	9.75	0.198
48	320	8.20	0.166
54	310	7.80	0.158
123	300	3.95	0.080

Mean velocity = 0.00163 gram-equivalent per hour.

The velocity in the two experiments is thus seen to be approximately proportional to the concentration of the baryta.

Velocity of saponification of nitroglycerine.—The nitroglycerine was suspended in 100 c.c. of baryta water, which was continuously agitated. From time to time, quantities of 10 c.c. were withdrawn and titrated, care being taken not to abstract any of the nitroglycerine.

Hydrolysis of Nitroglycerine by Baryta Solution.—Temp. = 39°. Quantity of nitroglycerine = 0.6670 gram. Initial volume of solution = 100 c.c.

Time in hours.	Volume of solution.	C.c. of 0.0970 normal acid required.	Concentration of baryta (gram- equiv. per litre).
0	100	8.35	0.0810
1	90	7.05	0.0684
2	80	6.25	0.0606
3	70	5.1	0.0495
4	60	3.6	0.0349
5.5	50	0.2	0.0019

The course of the saponification is shown in Fig. 1, and the velocity is seen to be much greater than that found in the case of gun-cotton.

On further standing the solution became neutral, but no acid reaction set in even after several days.

Hydrolysis of explosives containing both nitrocellulose and nitroglycerine.—Cordites and ballistites were taken for these experiments. They were ground and passed through a sieve of 0.85 mm. mesh, and 10 grams were taken for the hydrolysis, which was carried out at 39°.

1. *Cordite* No. 181.

Composition : Nitrocellulose (N = 12.75 per cent.)	36.26 per cent.
Nitroglycerine	58.85 „
Mineral jelly.....	4.76 „
Moisture and acetone	0.13 „

Time in hours.	Volume of solution.	C.c. of 0.2027 normal acid required.	Concentration of baryta (gram- equiv. per litre).
0	400	8.90	0.180
1	390	7.20	0.146
3	380	5.55	0.113
4	370	4.95	0.100
27	340	1.75	0.036
47	320	0.65	0.013
54	310	0.40	0.008

2. *Cordite* No. 202.

Composition : Nitrocellulose (N = 12.85 per cent.)...	37 per cent.
Nitroglycerine	58 „
Mineral jelly	5 „

0	400	9.40	0.191
1	390	6.70	0.136
2	380	5.80	0.118
3.5	370	5.10	0.103
5	360	4.65	0.094
6.5	350	4.15	0.084

3. *Ballistite*.

Composition : Nitrocellulose (N = 11.36 per cent.)	50.95 per cent.
Nitroglycerine	49.05 „

0	400	11.40	0.231
1	390	10.25	0.208
24	350	5.70	0.116
27	340	5.30	0.107
30	330	4.90	0.099
47	320	3.80	0.077
54	310	3.45	0.070
123	300	1.75	0.036

An analysis of the insoluble cordite which remained in the baryta after the saponification of cordite No. 202 had proceeded for some time showed that the hydrolysis was due almost entirely to nitroglycerine which had passed out of the powder into the aqueous solution.

The residue was dried at the ordinary temperature over sulphuric acid under diminished pressure. It was found to weigh 5·7811 grams, and gave on analysis :

Nitroglycerine, 29·32 ; nitrocellulose, 62·21 per cent.

Nitrogen in nitrocellulose, 12·99 per cent.

Total nitrogen, calculated from ingredients, 13·51 per cent.

Found 13·46 ,,

If the quantities of the different ingredients be compared before and after the saponification, the following figures are obtained :

	Before saponification.	After saponification.
Weight of explosive (grams)	10·00	5·78
Percentage of nitroglycerine	58	29·32
,, nitrocellulose	37	62·21
,, mineral jelly	5	8·47
Weight of nitroglycerine	5·80	1·70
,, nitrocellulose	3·70	3·60
,, mineral jelly	0·50	0·49

Thus it is seen that the nitrocellulose remained almost unaltered, whilst 70 per cent. of the nitroglycerine underwent hydrolysis.

Our thanks are due to the Explosives Committee and to the Director of Artillery for permission to publish these results, and to Mr. E. L. Lomax for his assistance in the work.

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CLXXII.—*Contributions to the Theory of Solutions.*

I. *The Nature of the Molecular Arrangement in Aqueous Mixtures of the Lower Alcohols and Acids of the Paraffin Series.* II. *Molecular Complexity in the Liquid State.* III. *Theory of the Intermiscibility of Liquids.*

By JOHN HOLMES.

WHEN two liquids which are miscible or partially miscible are allowed to intermingle, the volume of the mixture is invariably different from the sum of the initial volumes of its constituents. In some cases, as for instance when sulphuric acid or ethyl alcohol is mixed with water, a considerable contraction in volume occurs, whilst on the other hand when carbon disulphide is mixed with chloroform or ethyl alcohol, a small but appreciable expansion is obtained. Neither the specific volumes, therefore, nor the other physical properties of a mixture can be strictly classed as additive functions of the properties of the constituents, the only additive property being, according to the law of the indestructibility of matter, that of "mass."

With a view to ascertaining whether the deviations observed in the simple additive relations of liquids would throw any light on their molecular conditions, the differences in volume which occur on mixing the lower alcohols and acids of the paraffin series with water were calculated from already available data.

(1) *Mixtures of the Lower Primary Alcohols with Water.*

Graham (*Phil. Trans.*, 1861, 151, 373) pointed out that when ethyl alcohol and water are mixed together, the contraction in volume, when calculated as a percentage on the initial volumes, reaches a maximum at a point representing an admixture of one molecule of alcohol with three molecules of water. Mendeléeff (*Trans.*, 1887, 51, 778) states that the first differentials of the densities of these mixtures form a rectilinear figure showing three distinct breaks or transition points, one of which occurs when the constituents are mixed in the above proportions, viz., $C_2H_6O, 3H_2O$, whilst others occur at mixtures represented by $3C_2H_6O, H_2O$ and $C_2H_6O, 12H_2O$ respectively. From his observations on the behaviour of these and other aqueous mixtures, Mendeléeff put forward the

hypothesis that the specific gravities depend on the extent to which definite hydrates are produced and dissociated.

The following calculations were made in the case of ethyl alcohol and water, using Mendeléeff's data for the specific gravities of these mixtures (*Ann. Phys. Chem.*, 1869, ii, 138, 230).

Column I. gives the molecular proportions, referred to the gaseous state, in which the alcohol and water are mixed.

Column II. gives the actual contraction in c.c. when the volume of alcohol is kept constant at 100 c.c.

Column III. gives the contraction calculated as a percentage on the initial volumes.

Column IV. gives the difference between the percentage of alcohol by volume in the mixture and the theoretical percentage, assuming that no contraction occurs on mixing.

Volumes corrected to 15.56°.

I.	II.	III.	IV.
12C ₂ H ₆ O, H ₂ O	0.55 c.c.	0.51	0.53
11C ₂ H ₆ O, H ₂ O	0.60 „	0.59	0.57
10C ₂ H ₆ O, H ₂ O	0.66 „	0.61	0.62
9C ₂ H ₆ O, H ₂ O	0.73 „	0.70	0.69
8C ₂ H ₆ O, H ₂ O	0.81 „	0.78	0.76
7C ₂ H ₆ O, H ₂ O	0.91 „	0.87	0.84
6C ₂ H ₆ O, H ₂ O	1.04 „	0.99	0.95
5C ₂ H ₆ O, H ₂ O	1.21 „	1.14	1.08
4C ₂ H ₆ O, H ₂ O	1.45 „	1.34	1.26
3C ₂ H ₆ O, H ₂ O	1.80 „	1.63	1.51
2C ₂ H ₆ O, H ₂ O	2.41 „	2.09	1.85
C ₂ H ₆ O, H ₂ O	3.79 „	2.89	2.27
C ₂ H ₆ O, 1 $\frac{1}{4}$ H ₂ O	4.34 „	3.13	2.33
C ₂ H ₆ O, 1 $\frac{1}{2}$ H ₂ O	4.84 „	3.30	2.32
C ₂ H ₆ O, 1 $\frac{3}{4}$ H ₂ O	5.28 „	3.42	2.30
C ₂ H ₆ O, 2H ₂ O ..	5.69 „	3.51	2.24
C ₂ H ₆ O, 3H ₂ O	7.03 „	3.64	1.95
C ₂ H ₆ O, 4H ₂ O	7.94 „	3.54	1.64
C ₂ H ₆ O, 5H ₂ O	8.52 „	3.34	1.35
C ₂ H ₆ O, 6H ₂ O	8.87 „	3.09	1.11
C ₂ H ₆ O, 7H ₂ O ..	9.02 „	2.84	0.92
C ₂ H ₆ O, 8H ₂ O ..	9.08 „	2.61	0.77
C ₂ H ₆ O, 9H ₂ O	9.07 „	2.39	0.64
C ₂ H ₆ O, 10H ₂ O	8.99 „	2.19	0.55
C ₂ H ₆ O, 11H ₂ O	8.89 „	2.02	0.47
C ₂ H ₆ O, 12H ₂ O	8.78 „	1.86	0.40
C ₂ H ₆ O, 20H ₂ O	7.88 „	1.09	0.15
C ₂ H ₆ O, 40H ₂ O	6.79 „	0.54	0.04
C ₂ H ₆ O, 80H ₂ O	5.96 „	0.23	0.01
C ₂ H ₆ O, 320H ₂ O	5.30 „	0.05	—

It appears from column II. that the effect of each additional water molecule as regards contraction, gradually diminishes until the molecules are present in the proportion to form the aggregate C₂H₆O, 8H₂O, when the contraction reaches a maximum. The further addition of water results in a diminishing contraction,

which when 320 molecules have been added, representing a mixture containing less than one per cent. of alcohol, has not been reduced by one half, and is still greater than that obtained by mixing the molecules in equal proportions. Column III. shows that the maximum percentage contraction occurs when the ingredients are mixed in the proportion to form $C_2H_6O, 3H_2O$ (Mendeléeff's hydrate), whilst from column IV. the greatest difference between the percentage of alcohol (by volume) in the mixture and the theoretical percentage assuming no contraction occurs very near an admixture of equal proportions of molecules.

Similar calculations were made in the case of methyl alcohol and water from Dittmar and Fawsitt's data (*Trans. Roy. Soc. Edin.*, 1888, **33**, 509), and in the case of *n*-propyl alcohol and water from data supplied by Young and Fortey (*Trans.*, 1902, **81**, 726) and Pagliani (*Nuovo Cim.*, 1882, iii, **12**, 229).

The chief facts in connexion with the contractions of these three primary alcohols and water are as follows:—

Alcohol.	Ratio of the mole- cular volumes to that of water as unity at the same temperature.	Point at which the greatest contraction in volume occurs when increasing quantities of water are added to 100 c.c. alcohol.	Point at which the maximum percentage contrac- tion occurs, when calculated on the initial volumes.	Point at which the greatest difference occurs between the theoretical and ob- served percent- ages of alcohol by volume.
Methyl alcohol...	2·23	$CH_4O, 5H_2O$	$2CH_4O, 3H_2O$	CH_4O, H_2O
Ethyl „ ...	3·22	$C_2H_6O, 8H_2O$	$C_2H_6O, 3H_2O$	$C_2H_6O, 1\frac{1}{4}H_2O$
<i>n</i> -Propyl „ ...	4·07	$C_3H_8O, 15H_2O$	$C_3H_8O, 6H_2O$	$C_3H_8O, 1\frac{1}{2}H_2O$

It is evident from a study of these mixtures that the maxima are directly dependent on the relative volumes occupied by the respective molecules, and that the actual, as well as the percentage, contractions are merely mathematical deductions influenced on the one hand by the attractive forces in play between the molecules which determine the degree of contraction at mixtures of equal molecular volumes, and on the other by differences in specific gravity.

The direct dependence of these maxima on the relative molecular volumes must necessarily afford evidence in the study of the aggregations of molecules in the liquid state. Eotvos (*Ann. Phys. Chem.*, 1886, **27**, 452), and more recently Ramsay and Shields (*Phil. Trans.*, 1893, **184**, 647) have concluded from the rate of change of molecular surface energy with temperature that the above alcohols contain such aggregates. Whatever may be the complexity of the liquid molecule, however, in any particular instance, and whether we look on it as consisting wholly or partially of matter or energy,

we may assume, as regards its general character, that its free path is bounded by a spherical surface, the radius of which is constant for any molecule of the same substance at constant temperature and pressure. If two sets of molecules, therefore, are mixed together, one of which has an attraction for the other, but not sufficient to cause the loss of its own individuality and form a new compound, we can treat them in the same way as a mixture of electrically charged inelastic spheres, the volume of which is always different from the sum of the initial volumes.

Thus the addition of the relatively smaller water molecules to a fixed number of alcohol molecules will result in an increasing contraction, as each water molecule fits into the intramolecular spaces between the larger alcohol molecules, until approximately an equal number of molecules is present. Near this point the influence of contraction will reach a maximum as regards the proportions of the relatively larger alcohol molecules in the initial and final volumes. In the case of an infinite number of molecules, the actual point of maximum difference must depend on the difference in the radii of the two influential spheres, and the nearer this ratio approaches unity, the nearer will the maximum difference in volumes approach an admixture of equal molecular volumes. We have already seen that in the case of mixtures of the above alcohols with water, the specific gravities of which may be regarded as known within a very close approximation to accuracy, this point gradually recedes from the admixture of equal proportions of the molecules as the molecular volume increases. The further addition of water causes a rearrangement in the relative positions of the molecules, and instead of the two being symmetrically placed in adjacent positions, the water molecules now so arrange themselves as to surround completely each molecule of alcohol, the effect of each on the contraction diminishing with the dilution.

Now the results of Ramsay and Shields's observations in the case of the primary alcohols indicate that methyl alcohol is the most complex, and that the complexity diminishes as the series is ascended. If this is so it is inconceivable, assuming that the contractions are functions of the difference in molecular volumes, that the pivot, as it were, of the observed contractions of each of the alcohols with water should be the admixture of equal proportions of the molecules, as referred to the gaseous state. It would appear, therefore, as though the molecules of the above alcohols and water are either similar to their gaseous molecules, or, if aggregated, the degree of aggregation is the same in each alcohol as in water.

The phenomenon of contraction is not peculiar to mixtures of

alcohols and water alone, but is common, in some degree, to almost all liquids miscible or partially miscible with water, and appears to be directly related to the hygroscopic power of a substance—the evolution of heat (Young and Fortey in the case of the alcohols, *loc. cit.*) and the degree of contraction increasing in like proportion.

In the case of the primary alcohols, where the influence of contraction results in a density which is intermediate between the initial densities of the constituents of the mixture, it is found that when the volume of the constituent having the least density is made constant, the actual contraction reaches a maximum, and the further addition of the heavier constituent results in a diminishing contraction. When, however, the influence of contraction results in a density which is greater than that of either of the constituents, as in the case of mixtures of acetic or propionic acids with water, the continued addition of the one to the other set of molecules results in an ever-increasing contraction showing no indication of a maximum.

(2) *Mixtures of the Lower Fatty Acids with Water.*

With the exception of formic acid the lower fatty acids are peculiar, inasmuch as they form mixtures with water which possess densities greater than that of either constituent.

Thus acetic acid has a specific gravity 1.0497 at 20/4°, whereas a mixture containing 22 per cent. of water has at the same temperature a specific gravity of 1.0700, and this is a maximum for mixtures of these liquids (Oudemans, *Zeit. f. Chem.*, 1866, 5, 452).

Propionic acid has a specific gravity 0.9902 at 25/25°, and a maximum density (1.0250) occurs in aqueous solutions at a mixture containing 49.3 per cent. of water (Ludeking, *Ann. Phys. Chem.*, 1886, 27, 74).

n-Butyric acid has a specific gravity 0.9549 at 25/25°, and a maximum (1.0047) occurs at a mixture containing 80.4 per cent. of water (Ludeking, *loc. cit.*).

Formic acid, however, has a specific gravity 1.2213 at 20/4° (Richardson, *Amer. Chem. J.*, 1897, 19, 149), and forms mixtures which have densities intermediate between this and water; it therefore follows the same rule as was noticed in the case of the lower alcohols, and affords a point of maximum contraction when it is mixed with water in the proportion of (approximately) one molecule of water to nine of acid. The remaining acids, on the other hand, show increasing contractions when either the volume of acid or water is made constant.

Below is given a table of the contractions which occur when acetic acid is mixed with water, calculated in a similar manner to those given above in the case of the lower alcohols, and it is of interest inasmuch as the molecular volume of acetic acid (referred to the gaseous state) is almost identical with that of ethyl alcohol. Herein is shown the effect of difference in specific gravity on the contractions—both actual and percentage already referred to—but the maximum difference between the theoretical and observed percentages of acid (in column IV.) occurs as before at a mixture representing approximately equal molecular volumes of the constituents.

Columns I., II., III., and IV. have the same significance as in the case of the alcohols and water.

Volumes corrected to 20°.

I.	II.	III.	IV.
$12\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O} \dots\dots\dots$	0.71	0.70	0.68
$8\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O} \dots\dots\dots$	1.03	0.99	0.96
$4\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O} \dots\dots\dots$	1.75	1.62	1.53
$2\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O} \dots\dots\dots$	2.73	2.36	2.09
$1\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O} \dots\dots\dots$	3.57	2.85	2.34
$1\text{C}_2\text{H}_4\text{O}_2, \text{H}_2\text{O} \dots\dots\dots$	4.01	3.05	2.39
$\text{C}_2\text{H}_4\text{O}_2, 1\frac{1}{2}\text{H}_2\text{O} \dots\dots\dots$	4.44	3.18	2.36
$\text{C}_2\text{H}_4\text{O}_2, 2\text{H}_2\text{O} \dots\dots\dots$	5.47	3.35	2.13
$\text{C}_2\text{H}_4\text{O}_2, 3\text{H}_2\text{O} \dots\dots\dots$	6.38	3.28	1.74
$\text{C}_2\text{H}_4\text{O}_2, 4\text{H}_2\text{O} \dots\dots\dots$	7.05	3.11	1.42
$\text{C}_2\text{H}_4\text{O}_2, 5\text{H}_2\text{O} \dots\dots\dots$	7.52	2.92	1.17
$\text{C}_2\text{H}_4\text{O}_2, 6\text{H}_2\text{O} \dots\dots\dots$	7.89	2.73	0.97
$\text{C}_2\text{H}_4\text{O}_2, 7\text{H}_2\text{O} \dots\dots\dots$	8.18	2.55	0.81
$\text{C}_2\text{H}_4\text{O}_2, 8\text{H}_2\text{O} \dots\dots\dots$	8.42	2.39	0.69
$\text{C}_2\text{H}_4\text{O}_2, 9\text{H}_2\text{O} \dots\dots\dots$	8.60	2.24	0.59
$\text{C}_2\text{H}_4\text{O}_2, 10\text{H}_2\text{O} \dots\dots\dots$	8.77	2.11	0.52
$\text{C}_2\text{H}_4\text{O}_2, 11\text{H}_2\text{O} \dots\dots\dots$	8.88	1.98	0.45
$\text{C}_2\text{H}_4\text{O}_2, 12\text{H}_2\text{O} \dots\dots\dots$	8.99	1.88	0.40
$\text{C}_2\text{H}_4\text{O}_2, 13\text{H}_2\text{O} \dots\dots\dots$	9.09	1.78	0.35
$\text{C}_2\text{H}_4\text{O}_2, 14\text{H}_2\text{O} \dots\dots\dots$	9.18	1.69	0.32
$\text{C}_2\text{H}_4\text{O}_2, 15\text{H}_2\text{O} \dots\dots\dots$	9.24	1.61	0.29
$\text{C}_2\text{H}_4\text{O}_2, 16\text{H}_2\text{O} \dots\dots\dots$	9.33	1.54	0.26
$\text{C}_2\text{H}_4\text{O}_2, 32\text{H}_2\text{O} \dots\dots\dots$	9.80	0.88	0.08
$\text{C}_2\text{H}_4\text{O}_2, 64\text{H}_2\text{O} \dots\dots\dots$	10.01	0.47	0.02
$\text{C}_2\text{H}_4\text{O}_2, 128\text{H}_2\text{O} \dots\dots\dots$	10.47	0.25	0.01

The contractions in the case of formic, propionic and *n*-butyric acids are very similar in character. It is, however, the nature of the contractions around the mixture of equal molecular volumes which is of most interest, and these are set out below.

Molecular proportion.	Contraction in c.c. when the volume of acid is constant at 100 c.c.	Difference between the theoretical and observed percentages of acid by volume.
<i>Formic acid:</i>		
$2\text{H}_2\text{CO}_2, \text{H}_2\text{O}$	1.48	0.97
$1\frac{1}{2}\text{H}_2\text{CO}_2, \text{H}_2\text{O}$	1.93	1.12
$\text{H}_2\text{CO}_2, \text{H}_2\text{O}$	2.66	1.24
$\text{H}_2\text{CO}_2, 1\frac{1}{2}\text{H}_2\text{O}$	3.24	1.12
$\text{H}_2\text{CO}_2, 2\text{H}_2\text{O}$	3.79	1.01
<i>Propionic acid:</i>		
$2\text{C}_3\text{H}_6\text{O}_2, \text{H}_2\text{O}$	1.73	1.40
$1\frac{1}{2}\text{C}_3\text{H}_6\text{O}_2, \text{H}_2\text{O}$	2.46	1.80
$\text{C}_3\text{H}_6\text{O}_2, \text{H}_2\text{O}$	3.02	2.00
$\text{C}_3\text{H}_6\text{O}_2, 1\frac{1}{2}\text{H}_2\text{O}$	3.59	1.99
$\text{C}_3\text{H}_6\text{O}_2, 2\text{H}_2\text{O}$	4.03	1.89
<i>n-Butyric acid:</i>		
$2\text{C}_4\text{H}_8\text{O}_2, \text{H}_2\text{O}$	1.54	1.30
$1\frac{1}{2}\text{C}_4\text{H}_8\text{O}_2, \text{H}_2\text{O}$	1.83	1.42
$\text{C}_4\text{H}_8\text{O}_2, \text{H}_2\text{O}$	2.27	1.62
$\text{C}_4\text{H}_8\text{O}_2, 1\frac{1}{2}\text{H}_2\text{O}$	2.65	1.61
$\text{C}_4\text{H}_8\text{O}_2, 2\text{H}_2\text{O}$	2.96	1.56

It is seen, therefore, that, as in the case of the lower alcohols, the greatest difference between the percentage of acid in the contracted volumes and the theoretical percentage, assuming no contraction, occurs approximately at the point representing an admixture of equal molecular volumes.

These facts are only open to one interpretation, if we assume that the free path of a liquid molecule can be represented by a spherical surface. For, inasmuch as the weight of a liquid molecule must be identical with, or a simple multiple of, that of the gaseous molecule, it follows from the theory of spheres enunciated above that the molecular complexities of any mixture of molecules must be given by a comparison of the relative volumes which yield a maximum difference between the theoretical and observed proportions of the more active constituent. As we have seen that this maximum difference in the case of both the lower alcohols and fatty acids occurs when approximately equal proportions of the molecules, referred to the gaseous state, are mixed together, it follows that the molecular complexity of water is the same as that of each of the above liquids, and the existence of hydrates must be excluded from the theory of solutions.

Molecular Complexity in the Liquid State.

Few aqueous mixtures of organic liquids have been studied so thoroughly as those of the lower primary alcohols and fatty acids. The specific gravities of mixtures of acetone with water are, however, well known (McElroy, *Amer. Chem. J.*, 1894, **16**, 618) and its molecular complexity is found to be the same as that of water; on the other hand, glycerol (Nicol, *Pharm. J.*, 1887, **18**, 302), and nicotine (Pribram, *Sitzungsber. K. Acad. Wien*, 1897, **Ib**, **106**, 314) have only one half the aggregation.

The behaviour of acetone in aqueous solution is important from the fact that its molecular volume is almost the same as that of *n*-propyl alcohol, and the relative molecular weights and specific gravities are not very different. It was found that although the maximum difference between the theoretical and observed proportions of acetone by volume occurred at exactly the same molecular mixture as was noticed in the case of *n*-propyl alcohol and water, proving that it was similarly aggregated, the degree of contraction differed greatly. The actual contraction at this point in the case of acetone and water when the volume of acetone is taken as 100 was found to be 4.98 vols., whereas in the case of *n*-propyl alcohol it was only 2.66 vols. It is evident that the attraction of acetone for water is greater than that of *n*-propyl alcohol, but the fact also proves that the molecular volume of a liquid as determined from its molecular weight and specific gravity does not represent the true mean spherical path of the molecule. In other words, just as the volumetric changes accompanying the admixture of the primary alcohols, fatty acids, &c., with water can only be explained on the supposition that there are forces of attraction between the several molecules, so it is natural to expect that, as in the case of spheres similarly electrified, molecules of the same substance will repel each other. The degree of repulsion between individual molecules would thus vary with the chemical nature of the substance, and go far in explaining the volumetric changes in a mixture of liquids, such as benzene and chloroform, the volume of which after admixture is greater than the sum of the initial volumes.

The fact that the true relative volumes of liquid molecules are unknown does not vitiate the conclusions deduced from the above theory of spheres in regard to molecular complexities, but before this theory can be applied in a similar manner to liquids which exhibit a force of repulsion *inter se*, it becomes necessary to know on which molecule this increased force of repulsion on mixing depends, or, in other words, which is the more active molecule.

We are unable, for instance, from a study of mixtures of benzene and chloroform alone to draw any definite conclusions as regards the relative complexities of their molecules without knowing the complexity of one constituent in the mixture. Both liquids are, however, miscible in all proportions with ethyl ether, and a contraction in volume then occurs which is different in degree in each case. From the specific gravities of mixtures of ethyl ether and chloroform (Thorpe and Rodger, *Trans.*, 1897, **71**, 360) it is found that the greatest difference between the theoretical and observed percentages of chloroform by volume occurs when the molecules are mixed in the proportion of two of chloroform to one of ether, whilst similar calculations in the case of ethyl ether and benzene from Linebarger's data (*Amer. Chem. J.*, 1896, **18**, 429) show that the point of maximum difference in the percentage of benzene by volume occurs at a mixture of two molecules of benzene with one of ether (referred to the gaseous state). Benzene and chloroform, therefore, must be similarly aggregated.

These figures, however, do not by themselves prove that chloroform and benzene are doubly aggregated as compared with ethyl ether, for if in each series of mixtures we determine the points at which the greatest difference occurs between the theoretical and observed percentages by volume of ethyl ether, we obtain the reciprocal proportions, namely, two molecules of ether to one of chloroform or benzene.

The volumetric changes which occur in the case of most other mixtures of organic liquids of which we have any data are too small or unreliable to enable us to draw accurate conclusions regarding their molecular complexities. The following results were obtained in the case of those mixtures which yield differences in amount sufficient for the purpose.

Constituents of the mixture.		Molecular proportions at which the maximum difference occurs between the theoretical and observed percentages by volume of	
A.	B.	A.	B.
1. Chloroform	Ethyl ether ...	$2\text{CHCl}_3 - (\text{C}_2\text{H}_5)_2\text{O}$	$2(\text{C}_2\text{H}_5)_2\text{O} - \text{CHCl}_3$
2. Benzene	" " ...	$2\text{C}_6\text{H}_6 - (\text{C}_2\text{H}_5)_2\text{O}$	$2(\text{C}_2\text{H}_5)_2\text{O} - \text{C}_6\text{H}_6$
3. Carbon disulphide	Chloroform ...	$2\text{CS}_2 - \text{CHCl}_3$	$2\text{CHCl}_3 - \text{CS}_2$
4. " "	Benzene	$2\text{CS}_2 - \text{C}_6\text{H}_6$	$\text{C}_6\text{H}_6 - \text{CS}_2$
5. Ethyl ether	Methyl alcohol	$(\text{C}_2\text{H}_5)_2\text{O} - \text{CH}_3\text{OH}$	$2\text{CH}_3\text{OH} - (\text{C}_2\text{H}_5)_2\text{O}$

Data.

1. Thorpe and Rodger (*loc. cit.*).
2. Linebarger (*Amer. Chem. J.*, 1896, **18**, 429).
3. " " " "
4. " " " "
5. Centnerzwer and Zoppi (*Zeit. physikal. Chem.*, 1906, **54**, 690).

It is evident that from a consideration of the above figures alone we should have difficulty in assigning the relative degree of complexity to each of these several molecules. The complexity of any liquid, however, can be readily determined by mixing it with several members of a homologous series with which it is miscible in all proportions, provided that the volumetric changes are sufficient in amount, for when the liquid in question has the greater molecular volume, which implies in the generality of cases the more active molecule, the maximum difference between its theoretical and observed proportions in the mixtures must always occur at the same molecular admixture, whilst the maxima of the several homologues will vary with different members of the series, as is the case with water in its admixtures with the alcohols and acids.

In order to determine the degree of complexity of carbon disulphide in this manner, mixtures were made with ethyl and *n*-propyl alcohols, the specific gravities of which are set out below.

	Percentage of carbon disulphide by weight.	Specific gravity of the mixture at 15.5°/15.5°.
Carbon disulphide and ethyl alcohol	100.00	1.2713
	91.58	1.2057
	85.93	1.1664
	76.50	1.1071
	51.22	0.9758
	35.19	0.9089
	—	0.7940
Carbon disulphide and <i>n</i> -propyl alcohol	90.93	1.2043
	78.31	1.1243
	61.42	1.0342
	40.80	0.9436
	18.75	0.8644
	—	0.8080

In both cases heat was absorbed, and by interpolation of the small expansions thus obtained, it was found that the maximum difference between the theoretical and observed proportions of carbon disulphide by volume occurred at mixtures representing approximately four molecules of carbon disulphide with one of the alcohol (referred to the gaseous state). Accordingly the carbon disulphide molecule in the liquid state must be regarded as having a complexity four times that of the alcohol molecule. Since chloroform and benzene are similarly aggregated it follows from the above table that each has only one half the complexity of carbon disulphide, but twice that of ethyl ether, which latter is similarly aggregated to water and the alcohols.

Now Ramsay and Shields (*loc. cit.*) concluded from their experiments that the molecules of carbon disulphide, benzene, and ethyl ether were not aggregated as compared with those of water and the

alcohols, whereas the above results indicate a different degree of aggregation in the case of each liquid. Pyridine also was supposed to be less aggregated than water, and in order to test this statement according to the present theory mixtures were made with water and ethyl alcohol, and their densities determined. The boiling point of the sample of pyridine (Kahlbaum's) was $114-114.3^{\circ}$.

	Percentage of pyridine by weight.	Specific gravity of the mixture at $15.5^{\circ}/15.5^{\circ}$.
Pyridine and water	100.00	0.9880
	87.20	1.0016
	70.11	1.0111
	49.88	1.0115
	30.72	1.0088
	12.78	1.0046
Pyridine and ethyl alcohol	89.52	0.9651
	74.02	0.9328
	54.39	0.8939
	—	0.7940

In both cases heat was evolved, and from the curve of the relatively large contractions obtained the aggregation of pyridine in the liquid state was found to be the same as that of water and the alcohols.

The specific gravities of the mixtures of pyridine with water were also taken at 25° , but except that the contractions at corresponding concentrations were relatively smaller, no change was noticed in the points of maximum difference in the volumes of either constituent.

Theory of the Intermiscibility of Liquids.

When the primary alcohols and fatty acids are mixed with water it is found that the solubility decreases as we pass from the lower to the higher homologues. Methyl, ethyl, and *n*-propyl alcohols, for instance, are miscible in all proportions with water, whilst *n*-butyl- and amyl-alcohols have only a limited solubility. The same rule applies in the case of the fatty acids and other homologous series. As would be expected, when the aggregation is constant the molecular volumes also become greater with increase in molecular weight. This increased molecular volume, however, in the case of the higher homologues is probably far from representing the differences in the actual volumes occupied by the several molecules, and is rather to be explained by a greater force of repulsion between the molecules themselves as their mass increases, with a relative increase in the distance between the centres of mass of adjacent molecules. In fact, it is probable that the orbits of molecules of the most diverse substances in the liquid state do not differ greatly, and that the theory of spheres can be applied to the intermiscibility of liquids. What, therefore, is the essential difference

between the molecules of carbon disulphide and pyridine, benzene and nicotine, which decides their miscibility or immiscibility in water? A comparison of their molecular weights does not assist us, but when their molecular volumes are set out a remarkable series is obtained.

Below is given the relative molecular volumes (compared with that of water at the same temperature as unity) of some of the more commonly known organic liquids which have been dealt with above, (1) referred to the gaseous state, and (2) deduced from their ascertained complexities.

(1). Substance.	(2). Temperature.	(3). Molecular volume referred to the gaseous state. Water 1.	(4). Degree of aggrega- tion in liquid state. Water (H ₂ O) ₂ . Mol. wt.	(5). True molecular vol- ume deduced from the degree of complexity. Water 1.
Glycerol	20°	—	1	2·02
Formic acid	20	2·09	2	2·09
Methyl alcohol	15·5	2·27	2	2·27
Acetic acid.....	20	3·17	2	3·17
Ethyl alcohol	15·5	3·22	2	3·22
Carbon disulphide	20	3·34	8	—
Allyl alcohol	20	3·76	2	3·76
Lactic acid.,	20	4·02	2	4·02
Acetone	15	4·04	2	4·04
Glycerol	20	4·05	1	—
Propionic acid	0	4·06	2	4·06
<i>n</i> -Propyl alcohol	0	4·07	2	4·07
Chloroform	0	4·34	4	—
Pyridine	4	4·41	2	4·41
Nicotine	20	—	1	4·45
Benzene	20	4·91	4	—
<i>n</i> -Butyl alcohol	0	4·99	2	4·99
<i>n</i> -Butyric acid	19	5·08	2	5·08
Ethyl ether	4	5·62	2	5·62
<i>n</i> -Amyl alcohol.....	0	5·89	2	5·89
<i>n</i> -Caproic acid	22·7	6·93	2	6·93
Chloroform	0	—	4	8·68
Nicotine	20	8·90	1	—
Benzene	20	—	4	9·82
Lauric acid.....	44	12·60	2	12·60
Carbon disulphide.....	20	—	8	13·36

As will be seen from column 3 the gradual increase in molecular volume results in a decrease in miscibility with water only in the case of liquids having the same degree of complexity. Carbon disulphide and ethyl alcohol, for instance, have the same apparent molecular volume, whereas the one is insoluble in water and the other miscible in all proportions. When, however, the degree of aggregation in the liquid state is taken into consideration, carbon

disulphide takes its place at the bottom of the list in column 5, amongst the most insoluble substances.

Nicotine, on the other hand, from its apparently great molecular volume referred to the gaseous state, would be expected to be insoluble in water, but seeing that its complexity in the liquid state is only one-half that of water, it takes its place amongst the miscible substances. Glycerol, chloroform, and benzene in the same manner fall into their natural positions in column 5, so that we have here a series which, with the exception of *n*-butyl alcohol and *n*-butyric acid, show a decreasing solubility with increase in molecular volume.

Again, liquids adjacent to each other in this series and possessing molecular volumes within certain dimensions are mutually miscible. Thus glycerol is miscible with ethyl alcohol, but insoluble in ethyl ether; methyl alcohol is miscible with chloroform, but only partially miscible with carbon disulphide; pyridine, on the other hand, being near the limits of complete miscibility, is miscible with almost all the liquids mentioned from water to carbon disulphide.

Carbon disulphide, therefore, is insoluble whilst ethyl alcohol is easily miscible with water by reason of its relatively greater molecular volume. This explanation is, however, inadmissible without qualification, for we already know that the so-called molecular volume of a liquid does not represent the true spherical path of the molecule, otherwise *n*-butyric acid would be less soluble in water than *n*-butyl alcohol, whereas the reverse is the case. There is little doubt, however, that the mean path of a molecule can be represented by a spherical surface, and that it retains its individuality when mixed with other liquids; also that the so-called molecular volume is determined by forces of repulsion inherent to the molecules. Liquids, therefore, having approximate molecular volumes must mix together in the same way as a mixture of inelastic spheres, and this mutual miscibility will continue so long as the distance between the centres of mass of adjacent molecules is less than $\sqrt{(x+y)}$, where x and y are the radii of the spherical paths of individual molecules of each constituent. When the distance between the centres of mass of the molecules of either constituent becomes greater than this factor, mutual miscibility ceases, and the greater this factor, proportionately less miscible the liquids become, as in the case of spheres, the diameters of which are such as to allow the smaller to pass through the interstitial spaces of the larger spheres.

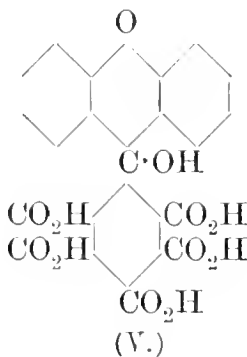
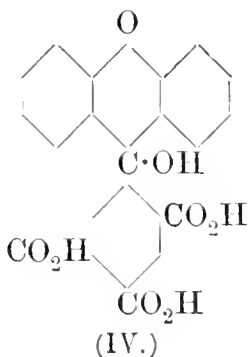
CLXXIII.—*The Relationship of Colour and Fluorescence to Constitution. Part I. The Condensation Products of Mellitic and Pyromellitic Acids with Resorcinol.*

By OSWALD SILBERRAD, Ph.D.

WHEN mellitic or pyromellitic acid is heated with phenols or meta-derivatives of phenols, condensation occurs, with the formation of colouring matters analogous to the phthaleins.*

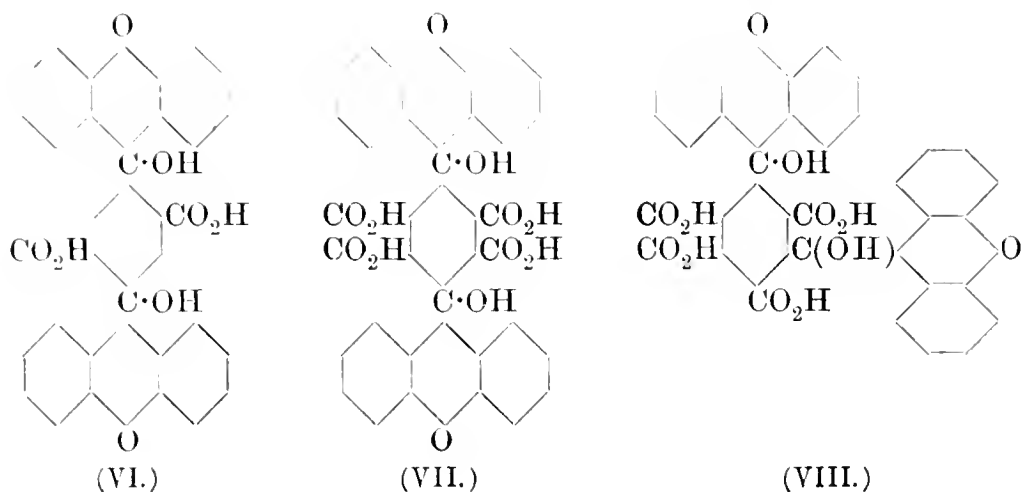
Mellitic acid is capable of forming three series of "melliteins," and similarly, pyromellitic acid can give rise to two series of derivatives. The general structure of the compounds follows from their method of preparation and their analogy to the phthaleins. It is convenient to classify them as mono-, di-, and tri-xanthyl derivatives.

The monoxanthyl derivatives obtained from pyromellitic acid may be regarded as being derived from 9-*hydroxyxanthylbenzene-2:4:5-tricarboxylic acid* (IV), and those obtained from mellitic acid as derived from 9-*hydroxyxanthylbenzene-2:3:4:5:6-pentacarboxylic acid* (V).

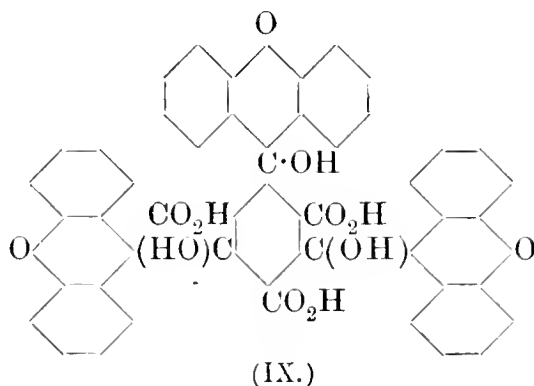


The dixanthyl compounds are similarly derived from 9:9'-*di-hydroxy-p-dixanthylbenzene-2:5-dicarboxylic acid* (VI), and 9:9'-*di-hydroxydixanthylbenzenetetracarboxylic acid* respectively. Of these, the former is derived from pyromellitic acid, and admits of only one isomeride, whilst the latter, derived from mellitic acid, occurs in two modifications, according as the xanthyl groups are para (VII) or meta (VIII) to one another.

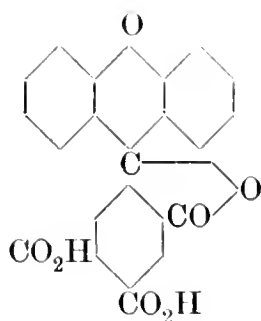
* The application of these compounds as dyestuffs has already been patented (Silberrad, Eng. Pat., No. 28638 of 1902).



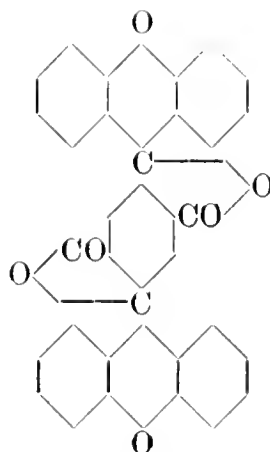
Derivatives of both the meta- and the para-compound have been prepared. They differ from one another in that the meta-compounds (VIII) are capable of condensing with a further pair of phenol molecules to form trianthyl derivatives. The parent compound of the trianthyl group is 9 : 9' : 9''-trihydroxytrianthylbenzenetricarboxylic acid (IX).



Anhydro-derivatives.—It is seen that the above carbinol derivatives are capable of losing water to form lactones. In the phthalein series, the carbinol derivatives are assumed to change spontaneously to lactones on passing from the ionised to the non-ionised condition. In the present study of the melliteins and pyromelliteins, it has been found that all the mellitic derivatives are hydrated and behave as though they contain the full complement of carboxylic acid groups as shown in formulæ (V), (VII), (VIII), and (IX). The pyromellitic derivatives, on the other hand, are anhydrides—presumably lactones—as represented in the formulæ (X) and (XI) :



(X.)

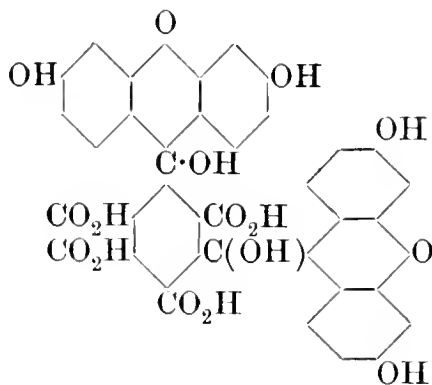


(XI.)

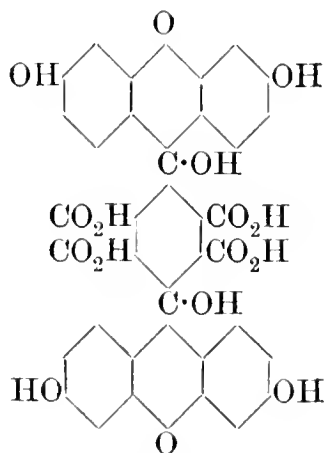
(X) 9-Hydroxyxanthylbenzene-2-carboxylactone-4 : 5-dicarboxylic acid,
and (XI) 9 : 9'-dihydroxydixanthylbenzene-2 : 5-dicarboxylactone.

*Orientation of the Xanthyl Groups in Dixanthyl Derivatives of
Mellitic Acid.*

In the mono- and tri-xanthyl derivatives the orientation of the xanthyl groups is not open to doubt; the dixanthyl compounds, however, are capable of existing in two modifications, according as the xanthyl groups are meta or para to each other, as shown in formulæ (XII) and (XIII). The ortho-position is excluded, as each xanthyl group requires the presence of two carboxylic groups, even although one of these is left intact.



(XII.)



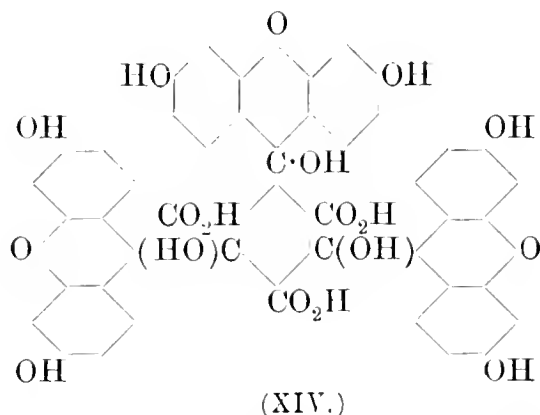
(XIII.)

(XII) Hexahydroxy-m-dixanthylbenzene-2:4:5:6-tetracarboxylic acid.

(XIII) Hexahydroxy-p-dixanthylbenzene-2:3:5:6-tetracarboxylic acid.

It is seen that only the meta-derivative is capable of combining with a further pair of resorcinol molecules to form nonahydroxy-sym-

trixanthylbenzenetricarboxylic acid, since two neighbouring carboxylic groups are necessary for the condensation with resorcinol. This property has been made use of for the orientation of these compounds. It is found that the ordinary hexahydroxydixanthylbenzenetetracarboxylic acid, obtained by direct condensation of resorcinol with mellitic acid, readily unites with a further pair of resorcinol molecules to form a trixanthyl derivative, namely :



(XIV) *Nonahydroxy-sym-trixanthylbenzene-2:4:6-tricarboxylic acid.*

The original compound must therefore have been the metadixanthyl derivative shown in formula (XII).

In order to prepare the para-isomeride, it is necessary to protect the 1:4-positions. This was accomplished by condensing 1:4-diethyl mellitate with resorcinol and subsequently saponifying the resulting ester. In this way, the para-compound (formula XIII) was obtained. This compound shows no tendency under any conditions to condense further with resorcinol. It will be observed that these derivatives of mellitic acid are hydrated, that is, the carboxylic acid groups adjacent to the xanthyl groups are unaffected, and it should therefore be possible to produce a hexaxanthyl derivative. This, however, has not been realised; it has been suggested that a pair of carboxylic acid groups adjacent, or in the ortho-position to one another, is necessary for the formation of a xanthyl ring. This, however, fails to account for the fact that the para-derivative, which still contains two pairs of ortho-carboxyl groups, does not form tri- and tetra-derivatives. The most logical explanation appears to be that the introduction of two xanthyl groups in adjacent positions is prevented by steric hindrance.

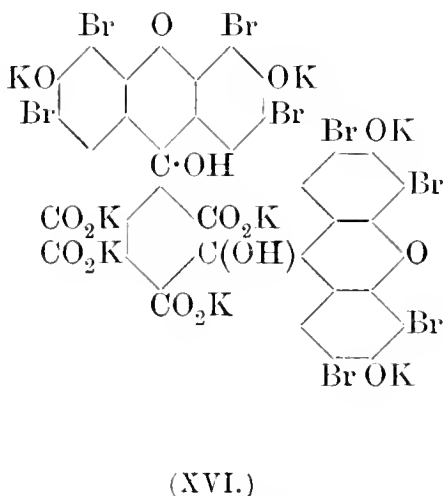
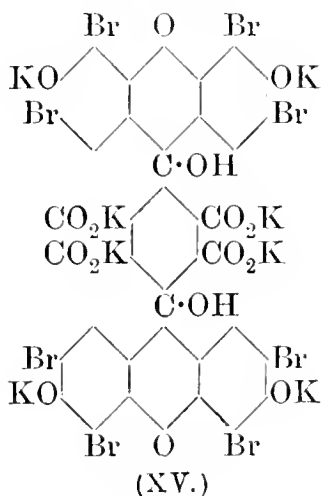
It is of interest to note that the two isomeric series of compounds show a distinct difference of colour. Thus 3:3':6:6':9:9'-hexahydroxy-*p*-dixanthylbenzene-2:3:5:6-tetracarboxylic acid dyes silk and wool a yellow ochre tint, whilst the meta-isomeride gives a brownish-yellow. The octabromo-derivatives of these two compounds show an equally marked difference of colour. The para-compounds

also show a much more intense fluorescence than the corresponding meta-derivatives.

Relationship of Constitution to Colour and Fluorescence.—Much of the interest of the present work lies in its bearing on the influence of constitution on colour and fluorescence. According to the ideas currently accepted, the colour and fluorescence of the phthaleins is attributed to a quinonoid structure of the molecule and to its oscillatory tautomeric relationship with the corresponding lactone. It is therefore a matter of surprise to find, as is shown in the present work, that many compounds of this class, although intensely coloured and strongly fluorescent, cannot reasonably be formulated as quinone derivatives and admit of no possibility of tautomerism. They should, indeed, according to the generally accepted theories, be colourless and non-fluorescent. Thus, the following are examples of compounds prepared in the present work which are saturated and contain neither lactone rings nor quinone groups and are incapable of tautomeric oscillation, yet they exhibit intense colour and fluorescence.

I. Haloid Derivatives of Di- and Tri-xanthyl Compounds.

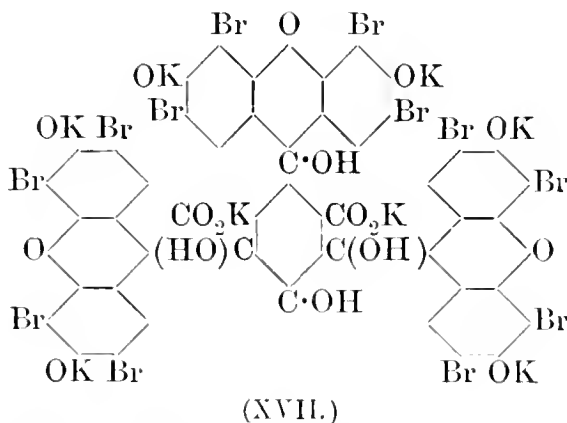
Examples of these are *octabrom-(or iodo)-3:3':6:6':9:9'-hexahydroxy-dixanthylbenzene-2:4:5:6-(or 2:3:4:5)-tetracarboxylic acids*. These compounds act as octabasic acids, forming well-defined and characteristic salts. The *potassium* salts, for example (formulae XV and XVI), are red powders possessing a metallic green reflex; they are very soluble in water, giving intense blood-red solutions which show a brown fluorescence, and dye silk and wool an intense pinkish-red.



(XV) *Potassium octabromohexahydroxy-p-dixanthylbenzene-2:3:5:6-tetracarboxylate.*

(XVI) *Potassium octabromohexahydroxy-m-dixanthylbenzene-2:4:5:6-tetracarboxylate.*

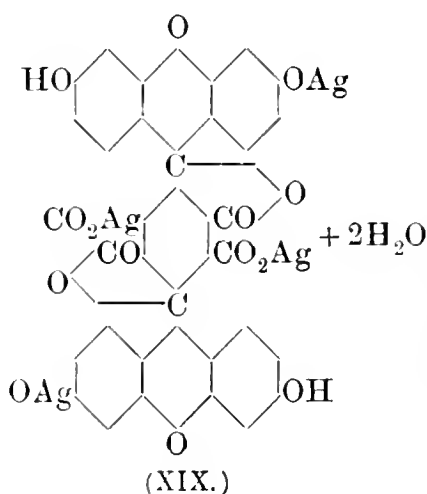
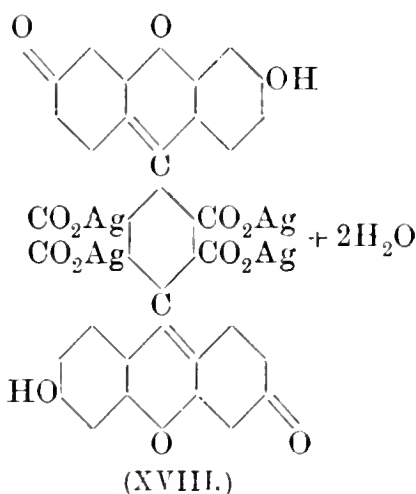
Dodecabromo- (and *iodo*)- *nonahydroxytrixanthylbenzenetricarboxylic acids* also belong to this class. They behave as nonabasic acids and yield well-defined salts, for example :



(XVII) *Potassium dodecabromononahydroxy-sym-trixanthylbenzene-2:4:6-tricarboxylate.*

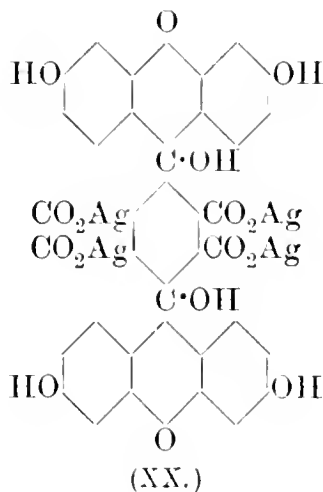
II. The Parent Hydroxy-compounds.

These possess precisely analogous structure, but in their case the basicity of the acid is restricted to the number of carboxylic groups present. This admits of the possibility of two methods of formulation apart from the above. Thus the silver salt, for example, of hexahydroxy-*p*-dixanthylbenzene-2:3:5:6-tetracarboxylic acid, that is, the parent compound corresponding to formula (XV), might be formulated either as (XVIII), or (XIX).



Since, however, the structure of the halogen derivatives has been placed beyond all doubt, and there are no grounds for assuming a difference of structure between these and the parent compounds, it appears that the latter also are saturated, as shown in the formula of *silver hexa-*

hydroxy-p-dixanthylbenzene-2 : 3 : 5 : 6-tetracarboxylate (XX), and contain neither lactonic nor quinonoid linkings.



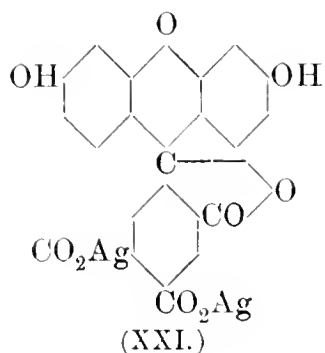
Notwithstanding the absence of all groups usually recognised as chromophores, these compounds are intensely coloured and show strong fluorescence. Further, it is seen that they are closely allied to the phthaleins themselves, thus the formation of derivatives which cannot be formulated so as to contain a quinonoid structure casts grave doubts on the presence of a quinone group in any of these compounds. Undoubtedly, in the instances cited above, another chromophore must be sought. The observations made in the present work appear to lend weight to Baeyer's theory of the constitution of phthaleins and other dyes (*Ber.*, 1905, 38, 569), according to which the colour is not due to a quinonoid structure but to a peculiar form of carbon linking. It certainly appears from the examples given that the 9-carbon atom of these xanthyl derivatives, which corresponds to the carbinol carbon atom of triphenylcarbinol compounds, possesses latent chromophoric properties, the development of which depends on the substituents in the xanthyl or other groups attached thereto.

Stability of the Lactone Ring in Phthaleins.—It is generally assumed that phenolphthalein and many of its derivatives exist in the form of lactones in the free state, but undergo a desmotropic change into quinone derivatives containing a carboxylic group in presence of alkali. According to this assumption, the lactone ring is supposed to be very labile, breaking open at once in presence of dilute alkali, whilst in fluorescent compounds the two formulæ are assumed to represent tautomeric compounds capable of constantly oscillating between the two configurations.

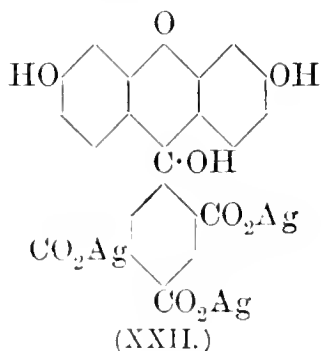
The present work gives indications that the change from the lactonic to the quinonoid structure frequently does not take place with the ease which has been generally assumed. In other cases, again, the com-

pounds show no tendency to pass into the lactonic form when liberated from their salts, but remain as carboxylic acids. Thus, in many instances the salt-formation occurs without any molecular rearrangement. The analogy between these compounds and the phthaleins is so close that a modification of the theory of these compounds may become necessary.

When trihydroxyxanthylbenzene-2-carboxylactonedicarboxylic acid is warmed with a quantity of caustic potash less than sufficient to dissolve it completely, and the excess of xanthyl compound separated, the solution yields on precipitation *silver trihydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylate* (XXI). Thus the compound acts as a

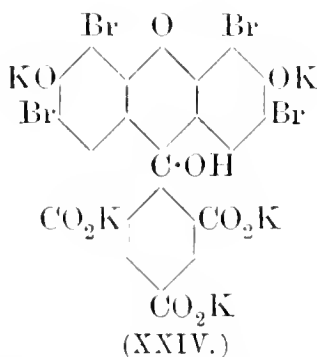
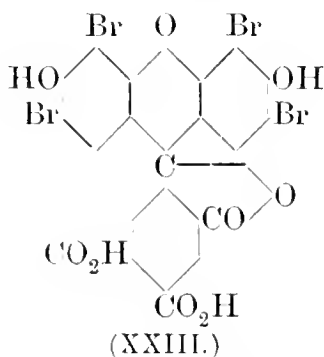


dibasic acid in these circumstances, indicating that the lactone ring does not break open so easily as is generally believed. If, however, the dipotassium salt is dissolved in water, and treated with a drop of caustic potash, a marked change of colour occurs. The solution, which was originally a bright orange, becomes much darker, more intensely coloured, and the fluorescence increases considerably. This evidently indicates that the lactone ring is broken open in presence of caustic alkali. Indeed it was found possible to precipitate *silver trihydroxyxanthylbenzene-2:4:5-tricarboxylate* (XXII) from a solution prepared by



treating one molecule of the xanthyl compound with three molecules of caustic potash. It will be observed that the salts corresponding to formula XXII are fully saturated compounds and cannot be formulated as quinone derivatives, unless a molecule of water is considered

as water of crystallisation. It is noteworthy that the tri-metallic salts show a much more brilliant metallic reflex and possess a much more intense colour and fluorescence in solution than the di-metallic salts, that is to say, the colour and fluorescence are strongest in the compounds which, according to the ideas hitherto accepted, contain no chromophore and do not admit of tautomerism, and should therefore be colourless and devoid of fluorescence. The haloid derivatives of the above compound are also lactonic (XXIII), but in this case the lactone ring readily opens on treatment with alkalis as above, and the compound acts as a pentabasic acid.



(XXIII) *Tetrabromotrihydroxyxanthylbenzenecarboxylactonedicarboxylic acid.*

(XXIV) *Potassium tetrabromotrihydroxyxanthylbenzenetricarboxylate.*

The results recorded in the present paper may be summarised as follows :

(1) Mellitic and pyromellitic acids condense with resorcinol to form a series of coloured compounds analogous to the phthaleins.

(2) Neither the colour nor the fluorescence of these compounds is dependent on the presence of quinone linkings, for in many instances a quinonoid structure is impossible.

(3) The change from a lactonic to a quinonoid structure, and *vice versa*, does not appear to take place with the ease which is generally assumed.

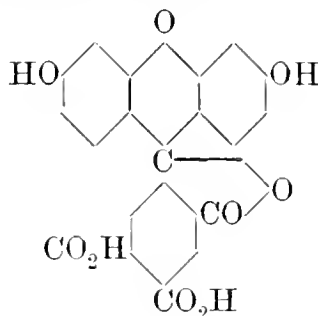
EXPERIMENTAL.

[With CHARLES SMART ROY.]—For the conversion of mellitic into pyromellitic acid the following conditions were found, after a series of experiments, to give the most favourable results. Fifty grams of mellitic acid are mixed with 80 grams of potassium hydrogen sulphate and made up into a thick paste with sulphuric acid. The mixture is heated to 200° for six hours and then distilled in a retort fitted with a long air condenser dipping into a receiver, so that when a little sulphuric acid has distilled over the vapours must bubble through it.

The decomposition gases carry over a considerable quantity of pyromellitic acid; this is collected by passing the vapour through cold water. White fumes are evolved at first, and after a time sulphuric acid passes over. Toward the end of the distillation the pyromellitic acid distils over in considerable quantity, and care must be taken to avoid choking of the condenser. The distillation is continued until no more acid passes over. The water and sulphuric acid, in which a portion of the pyromellitic acid has collected, are mixed and cooled to allow the dissolved acid to crystallise out. The acid is purified by recrystallisation from water. The yield amounts to 54 per cent.

I. Monoxanthyl Derivatives.

3 : 6 : 9-Trihydroxyxanthylbenzene-2-carboxylactone-4 : 5-dicarboxylic Acid (*Diresorcinolpyromellitein*), $C_{22}H_{12}O_9$.—This is prepared by heat-



ing a finely ground mixture of equal parts of pyromellitic acid and resorcinol to 160° for six hours. The mixture, which at first melts, gradually loses water and solidifies. When cold, the dark brown mass is powdered, extracted with boiling water, and the residue dissolved in a small quantity of alcohol. By this treatment a small quantity of a red organic compound insoluble in cold alcohol is removed. It is suggested that this may be the corresponding anthraquinone derivative. The anhydroxanthyl product is isolated and purified by fractional precipitation of its alcoholic solution by the addition of water. On analysis:

I.*	0.2230	gave	0.5154	CO_2	and	0.0521	H_2O .	C = 63.03 ;	H = 2.59.
II.	0.2157	,,	0.4974	CO_2	,,	0.0528	H_2O .	C = 62.89 ;	H = 2.72.
II.	0.1898	,,	0.4375	CO_2	,,	0.0469	H_2O .	C = 62.86 ;	H = 2.74.
III.	0.2091	,,	0.4800	CO_2	,,	0.0555	H_2O .	C = 62.60 ;	H = 2.94.
Mean C = 62.85 ; H = 2.77.									

$C_{22}H_{12}O_9$ requires C = 62.72 ; H = 2.87 per cent.

The substance is a bright yellow, amorphous powder melting at above 300° . It dyes silk and wool a brilliant yellow. It is insoluble

* These numerals refer to the different preparations.

in benzene, ether, or chloroform, and very slightly soluble in concentrated hydrochloric acid or water, giving in the latter solvent a very faint pink coloured solution having a most intense green fluorescence. It is fairly soluble in aniline, phenol, ethyl acetate, glacial acetic acid, or concentrated sulphuric acid, readily so in acetone or alcohol, in which solvents it gives a reddish-orange coloured solution having an intense green fluorescence; it is precipitated from these solvents on addition of water.

The compound dissolves readily in dilute aqueous caustic potash and ammonia, giving deep orange solutions having an intense green fluorescence; on acidifying these solutions, the acid is precipitated.

The alkali salts were prepared by warming a solution of caustic alkali with excess of the xanthyl compound, and after separating the excess of the latter, evaporating the filtrate. The salts of the heavy metals were obtained from the potassium salts by double decomposition.

The *lithium* and *potassium* salts are dark orange-red powders having a green metallic reflex.

The *silver* salt, $C_{22}H_{10}O_9Ag_2$, is a bright orange-red powder which is fairly stable to heat. It is readily soluble in ammonia; dilute nitric and glacial acetic acids dissolve the salt, precipitating out the free acid. On analysis:

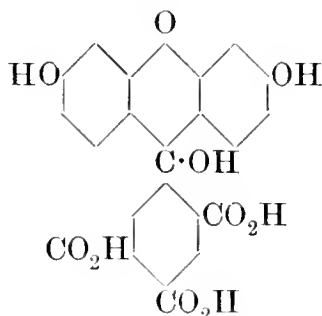
Preparation	I.	0.2176	gave 0.0744 Ag.	Ag = 34.19.
„	II.	0.2757	„ 0.0942 Ag.	Ag = 34.16.
„	II.	0.2327	„ 0.0795 Ag.	Ag = 34.16.
„	III.	0.5219	„ 0.1771 Ag.	Ag = 33.93.
Mean Ag = 34.11.				

$C_{22}H_{10}O_9Ag_2$ requires Ag = 34.05 per cent.

The *copper*, *cobalt*, *lead*, *ferrous*, and *chromium* salts are formed as orange precipitates.

The *ferric* salt is a dark brownish-red powder.

3 : 6 : 9-Trihydroxyxanthylbenzene-2 : 4 : 5-tricarboxylic Acid, $C_{22}H_{14}O_{10}$.



This acid does not exist in the free state; on liberation from its salts it at once loses water, yielding 3 : 6 : 9-trihydroxyxanthylbenzene-2-

carboxylactone-4:5-dicarboxylic acid. The *potassium* salt is obtained by suspending 2.1 parts of 3:6:9-trihydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylic acid in water and adding 0.838 parts of potassium hydroxide. After about 0.6 part has been run in, additional alkali causes a marked increase in colour and fluorescence. On evaporating the solution, the salt separates as a dark red powder having a bright olive-green, metallic reflex. It is very soluble in water, giving a brownish-red solution having a very intense green fluorescence. The *lithium* and *sodium* salts closely resemble the potassium salt.

The *silver* salt, $C_{22}H_{11}O_{10}Ag_3$, is a dark crimson powder having an olive-green, metallic reflex. It dissolves instantly in ammonia: dilute nitric and glacial acetic acids dissolve the salt, precipitating the lactonedicarboxylic acid. It is fairly stable to heat and light. On analysis:

I.*	from sodium salt	0.2371	gave	0.1001	Ag.	Ag = 42.22.
II.	„ sodium salt	0.1285	„	0.0546	Ag.	Ag = 42.49.
II.	„ sodium salt	0.1918	„	0.0814	Ag.	Ag = 42.44.
III.	„ lithium salt	0.1278	„	0.0544	Ag.	Ag = 42.56.
III.	„ lithium salt	0.1142	„	0.0485	Ag.	Ag = 42.46.
						Mean Ag = 42.43.

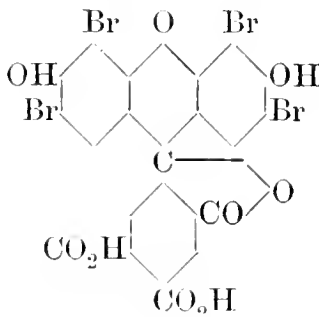
$C_{22}H_{11}O_{11}Ag_3$ requires Ag = 42.66 per cent.

The *copper* salt is a reddish-brown powder which turns dark brown on addition of ammonia.

The *cobalt* and *mercuric* salts are orange-red powders.

The *lead*, *chromium*, *ferrous*, and *ferric* salts are bright reddish-orange, dark yellowish-orange, brown, and dark brownish-red powders respectively.

2:4:5:7-Tetrabromo-3:6:9-trihydroxyxanthylbenzene-2-carboxylactone-4:5-dicarboxylic Acid (*Tetrabromodiresorcinolpyromellitein*), $C_{22}H_8O_9Br_4$.



The foregoing compound is dissolved in alcohol, cooled, and a slight excess of bromine slowly added. After twenty-four hours the mixture

* See footnote on p. 1796.

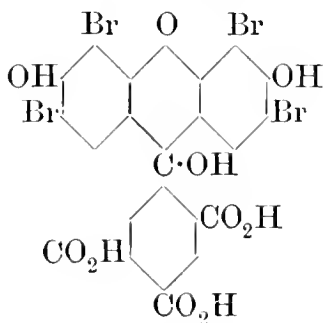
is thrown into water, the precipitate of the bromo-compound separated, and purified by exhaustive fractional precipitation of its alcoholic solution by the addition of water. On analysis :

Preparation	I.	0.5359	gave	0.5498	AgBr.	Br = 43.66.
„	II.	0.3124	„	0.3199	AgBr.	Br = 43.57.
„	III.	0.2209	„	0.2268	AgBr.	Br = 43.69.
„	IV.	0.2098	„	0.2134	AgBr.	Br = 43.28.
						Mean Br = 43.55.

$C_{22}H_8O_9Br_4$ requires Br = 43.46 per cent.

The substance is a bright orange-red, amorphous powder melting at 186—189°, and dyes silk and wool a brilliant crimson. It is insoluble in water, benzene, ether, chloroform, or concentrated hydrochloric acid, but slightly soluble in concentrated sulphuric and acetic acids, from which it is precipitated on dilution. It is fairly soluble in ethyl acetate and readily so in warm aniline, giving a fine deep red solution having a brown fluorescence; on cooling, the colouring matter separates. It is also soluble in phenol, acetone, or alcohol, giving deep red solutions from which the compound is precipitated on dilution with water. It dissolves in dilute potassium hydroxide or ammonia, with rupture of the lactone ring. The solutions have a fine deep red colour and a brown fluorescence.

2 : 4 : 5 : 7-Tetrabromo-3 : 6 : 9-trihydroxyxanthylbenzene-2 : 4 : 5-tri-



carboxylic Acid, $C_{22}H_{10}O_{10}Br_4$.—This acid is known only in the form of its metallic salts. When liberated it at once loses water, and is converted into *tetrabromotrihydroxyxanthylbenzenecarboxylactonedicarboxylic acid*.

The salts are prepared from the preceding lactone by the addition of alkali, which breaks open the lactone ring. The *sodium* and *lithium* salts are dark red powders having a very brilliant green metallic reflex, and are very readily soluble in water.

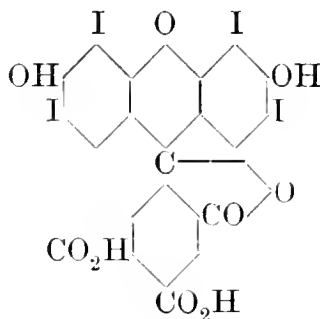
The *silver* salt, $C_{22}H_5O_{10}Br_4Ag_5$, is precipitated as a bright crimson precipitate which is fairly stable to heat and light, and is readily soluble in ammonia. Dilute nitric and glacial acetic acids dissolve the salt and precipitate the acid. On analysis :

Preparation	I.	0.5819	gave	0.4204	AgBr.	Ag = 41.50.
„	II.	0.3451	„	0.2522	AgBr.	Ag = 41.98.
„	II.	0.1998	„	0.1461	AgBr.	Ag = 42.00.
„	III.	0.2189	„	0.1600	AgBr.	Ag = 41.98.
„	IV.	0.1859	„	0.1349	AgBr.	Ag = 41.68.
						Mean Ag = 41.83.

$C_{22}H_5O_{10}Br_4Ag_5$ requires Ag = 41.88 per cent.

The *copper*, *barium*, *cobalt*, *lead*, *ferrous*, and *chromium* salts are formed as blood-red powders, the barium and copper salts being unaltered by ammonia; the *ferric* salt is a dull brownish-red powder.

2 : 4 : 5 : 7-Tetraiodo-3 : 6 : 9-trihydroxyxanthylbenzene-2-carboxylactone-4 : 5-dicarboxylic Acid (*Tetraiododiresorcinolpyromellitein*), $C_{22}H_8O_9I_4$.



Eight grams of trihydroxyxanthylbenzenecarboxylactonedicarboxylic acid are dissolved in 30 c.c. of a 20 per cent. caustic potash solution. This solution is boiled, and to it a boiling solution of 50 grams of iodine in 100 c.c. of 10 per cent. caustic potash is slowly added. The whole is then boiled for ten minutes and allowed to cool, when the iodo-compound separates out and is filtered off, washed thoroughly with hot water, dissolved in dilute caustic potash, and fractionally precipitated by addition of hydrochloric acid. On analysis:

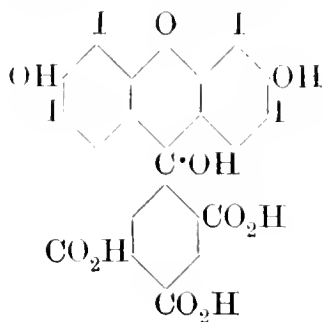
Preparation	I.	0.3855	gave	0.3918	AgI.	I = 54.93.
„	II.	0.2554	„	0.2608	AgI.	I = 55.20.
„	III.	0.2459	„	0.2520	AgI.	I = 55.39.
						Mean I = 55.17.

$C_{22}H_8O_9I_4$ requires I = 54.96 per cent.

This substance is a dark red, amorphous powder, which decomposes without melting at 187° with evolution of vapours of iodine. It is insoluble in water, concentrated hydrochloric acid, and nearly all organic solvents, but slightly soluble in concentrated sulphuric acid, giving a light brown solution; on dilution with water, the red colour appears, and the iodo-compound is precipitated. It is fairly soluble in alcohol, giving a bright red solution, and readily so in dilute alkalis

or ammonia, the lactone ring being thereby broken, and salts of the acid described below being formed. The solutions have a fine deep red colour, and on addition of hydrochloric acid the above lactonic acid is obtained.

2 : 4 : 5 : 7-Tetraiodo-3 : 6 : 9-trihydroxyxanthylbenzene-2 : 4 : 5-tricarboxylic Acid, $C_{22}H_{10}O_{10}I_4$.



This acid, like the corresponding bromo-derivative, exists only in the form of its salts. When liberated from these, it loses water and forms the preceding lactone.

The salts are prepared from the lactone described above by the addition of alkali, which breaks open the lactone ring.

The *lithium* and *potassium* salts are dark red powders having a brilliant green, metallic reflex.

The *silver* salt, $C_{22}H_5O_{10}I_4Ag_5$, is a blood-red powder soluble in ammonia. Glacial acetic and dilute nitric acids dissolve it and precipitate the lactone. On analysis :

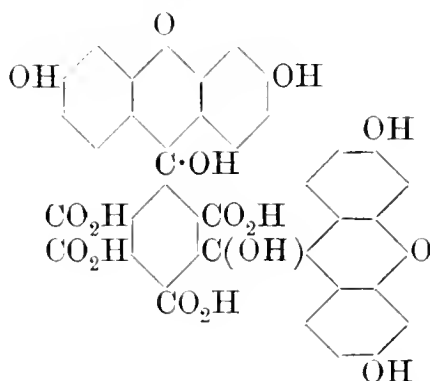
Preparation	I.	0.2020	gave	0.1617	Ag.	Ag = 36.78.
„	II.	0.2151	„	0.1718	Ag.	Ag = 36.69.
„	II.	0.1891	„	0.1509	Ag.	Ag = 36.66.
„	III.	0.1910	„	0.1526	Ag.	Ag = 36.70.
						Mean Ag = 36.71.

$C_{22}H_5O_{10}I_4Ag_5$ requires Ag = 36.54 per cent.

The *copper*, *barium*, *cobalt*, *lead*, *ferrous*, and *chromium* salts are blood-red powders, the copper and barium salts being unaltered by ammonia. The ferrous salt is dark orange-red.

II. *Dicanthyl Derivatives.*

3 : 3' : 6 : 6' : 9 : 9' - *Hexahydroxy-m-dicanthylbenzene-2 : 4 : 5 : 6-tetracarboxylic Acid* (*Tetraresorcinol-mellitein*), $C_{36}H_{22}O_{16}$,



is prepared by heating a finely-powdered mixture of 12.5 parts of mellitic acid and 8 parts of resorcinol to 160° for eight hours. After cooling, the mass is boiled with water and filtered, the residue being dissolved in alcohol, filtered, and the condensation product precipitated from the alcoholic solution by dilution with water. The precipitate is separated and purified by repeated fractional precipitation from its alcoholic solution by addition of water, the purified product being dried at 100° . On analysis :

- I.* 0.1112 gave 0.2488 CO_2 and 0.0319 H_2O . C = 61.02 ; H = 3.19.
 II. 0.2887 „ 0.6421 CO_2 „ 0.0855 H_2O . C = 60.65 ; H = 3.29.
 III. 0.1190 „ 0.2660 CO_2 „ 0.0353 H_2O . C = 60.96 ; H = 3.29.
 Mean C = 60.88 ; H = 3.26.

$C_{36}H_{22}O_{16}$ requires C = 60.83 ; H = 3.12 per cent.

The substance is a dark yellow, amorphous powder which decomposes above 300° without melting and dyes silk and wool a brownish-yellow. It is insoluble in cold water, ether, benzene, or chloroform, slightly soluble in boiling water, ethyl acetate, phenol, or concentrated hydrochloric acid, and fairly so in glacial acetic acid, from which solution it is precipitated on dilution with water. It is very soluble in acetone, giving a red solution, from which the acid is not readily precipitated on dilution with water. The substance is readily soluble in aniline or alcohol, giving reddish-brown solutions having an intense green fluorescence. On diluting the alcoholic solution with water, the acid is precipitated. It is also readily soluble in concentrated sulphuric acid, and is precipitated unchanged on dilution.

In dilute potassium hydroxide or ammonia it is exceedingly soluble,

* See footnote on p. 1796.

giving reddish-brown solutions having a most intense green fluorescence even when extremely dilute. From these solutions the acid is precipitated on acidifying.

The *ammonium* salt, prepared by adding excess of ammonia to the acid suspended in water, boiling, filtering, and evaporating the solution to dryness, first on the water-bath and finally in a vacuum desiccator over concentrated sulphuric acid, is a brownish-yellow powder readily soluble in water.

The *lithium* and *potassium* salts were prepared by boiling an excess of the acid with dilute aqueous solutions of the alkalis, separating the unchanged acid, and evaporating the solutions to dryness on the water-bath. These salts are dark reddish-brown powders having a green, metallic reflex. They are readily soluble in water, and the solutions have an intense green fluorescence.

The *silver* salt, $C_{36}H_{18}O_{16}Ag_4$, is a yellowish-orange precipitate which is fairly stable to heat and light. It is soluble in ammonia; dilute nitric acid and glacial acetic acid dissolve the salt with separation of the acid. On analysis:

Preparation I. 0.2137 gave 0.0814 Ag. Ag = 38.09.

„ II. 0.2579 „ 0.0983 Ag. Ag = 38.11.

Mean Ag = 38.10.

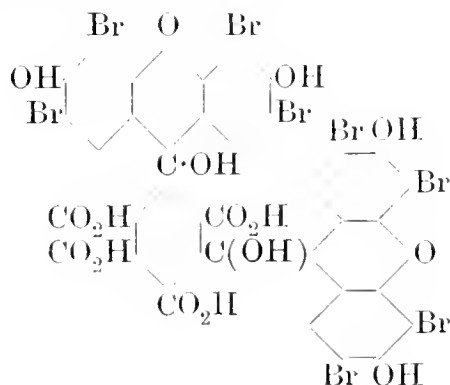
$C_{36}H_{18}O_{16}Ag_4$ requires Ag = 37.94 per cent.

The *copper*, *lead*, and *mercuric* salts are precipitated as yellowish-orange powders.

The *barium* salt is a light yellow powder slightly soluble in water; on addition of ammonia the colour becomes darker.

The *cobalt*, *ferric*, and *ferrous* salts are dark reddish-orange powders.

2:2':4:4':5:5':7:7'-Octabromo-3:3':6:6':9:9'-hexahydroxy-m-di-xanthylbenzene-2:4:5:6-tetracarboxylic Acid (Octabromotetrarresorcinol-mellitein), $C_{36}H_{14}O_{16}Br_8$.



The foregoing compound is suspended in glacial acetic acid and an excess of bromine gradually added. After allowing the mixture to

stand for 24 hours, it is heated on a water-bath for an hour, allowed to cool, and poured into a large quantity of water. The light red bromo-compound is separated and washed thoroughly with boiling water, dissolved in as small a quantity of alcohol as possible, filtered, and the alcoholic solution poured into water. The octabromo-derivative is precipitated from alcohol as a deep red, amorphous precipitate which is purified by fractional precipitation. On analysis:

Preparation I. 0.2065 gave 0.2307 AgBr. Br = 47.54.

„ II. 0.2173 „ 0.2432 AgBr. Br = 47.61.

Mean Br = 47.58.

$C_{36}H_{14}O_{16}Br_8$ requires Br = 47.68 per cent.

It is a dark orange-red, amorphous powder, which on rapid heating commences to decompose at 205°. It dyes silk and wool pink. It is insoluble in water, benzene, chloroform, or hydrochloric acid, but slightly soluble in ether or ethyl acetate, and easily so in acetone, phenol, aniline, or alcohol. The alcoholic solution is deep red, and shows an intense brown fluorescence; on dilution with water the acid is precipitated. The substance is fairly soluble in glacial acetic acid or concentrated sulphuric acid, from which solutions it is precipitated on dilution. It dissolves readily in dilute potassium hydroxide or ammonia, giving a deep blood-red solution having a brown fluorescence; from these solutions the compound is precipitated on acidification.

The *potassium* salt is a bright red powder having a bronzy-green, metallic reflex. The *lithium* salt is a deep red powder having a bronze reflex. The *silver* salt, $C_{36}H_6O_{16}Br_8Ag_8$, is a deep red powder which is fairly stable to heat and light. It is insoluble in water, but dissolves instantly in ammonia. Dilute nitric or glacial acetic acids dissolve the salt with separation of the acid. On analysis:

Preparation I. 0.3661 gave 0.2518 AgBr. Ag = 39.50.

„ II. 0.3390 „ 0.2328 AgBr. Ag = 39.44.

„ III. 0.2131 „ 0.1467 AgBr. Ag = 39.54.

„ IV. 0.1812 „ 0.1236 AgBr. Ag = 39.18.

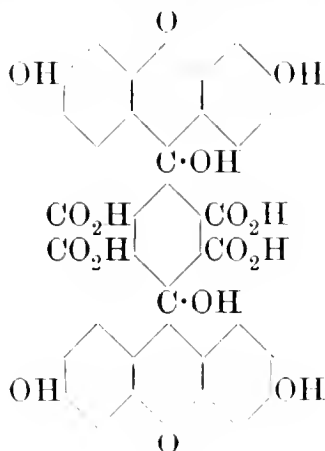
Mean Ag = 39.42.

$C_{36}H_6O_{16}Br_8Ag_8$ requires Ag = 39.30 per cent.

The *barium*, *lead*, *cobalt*, *copper*, *ferrous*, and *chromium* salts are precipitated as bright red powders, the barium and copper salts being unaltered by ammonia.

The *ferric* salt is obtained as a brownish-red, gelatinous precipitate.

3 : 3' : 6 : 6' : 9 : 9'-Hexahydroxy-*p*-dicanthylbenzene-2 : 3 : 5 : 6-tetracarboxylic Acid (Tetraresorcinol-mellitein), $C_{36}H_{22}O_{16}$.



This is prepared by heating 16 parts of *p*-diethyl mellitate with 17.6 parts of resorcinol to 150° for 8 hours. The hard mass is powdered, dissolved in concentrated aqueous caustic potash, and heated on the steam-bath for 3 hours to saponify the ester.

The solution is neutralised with hydrochloric acid, evaporated to dryness, and the residue extracted with alcohol. The condensation product is precipitated from its alcoholic solution by water and purified by repeated fractional precipitation. On analysis :

- I.* 0.1698 gave 0.3790 CO_2 and 0.0500 H_2O . C = 60.87 ; H = 3.30.
 II. 0.2153 „ 0.4816 CO_2 „ 0.0628 H_2O . C = 61.00 ; H = 3.24.
 Mean C = 60.94 ; H = 3.27.

$C_{36}H_{22}O_{16}$ requires C = 60.83 ; H = 3.12 per cent.

The substance is a dark yellowish-orange, amorphous powder, decomposing without melting above 300° , and dyes silk and wool yellow. It is insoluble in ether, benzene, or chloroform, slightly soluble in phenol, ethyl acetate, or concentrated hydrochloric acid, giving light reddish-brown solutions, and in water giving a light yellow solution having a most intense green fluorescence. It is fairly soluble in aniline or glacial acetic acid, giving deep red solutions, and exceedingly so in acetone or alcohol, giving with the latter a reddish-brown solution having an intense green fluorescence ; on addition of water to a concentrated solution the acid is precipitated. The compound is also soluble in dilute caustic alkali or ammonia, the solutions having an intense green fluorescence. On acidifying these solutions the acid is precipitated.

The *ammonium* salt is a dark brown powder having a dark green metallic reflex.

* See footnote on p. 1796.

The *potassium* and *lithium* salts are very dark reddish-brown powders having a dark green, metallic reflex. They are very soluble in water, giving reddish-brown solutions.

The *silver* salt, $C_{36}H_{18}O_{16}Ag_4$, is a reddish-orange powder, having a nearly black, metallic reflex. It is fairly stable to heat and light, and dissolves instantly in ammonia. Dilute nitric or glacial acetic acids dissolve the salt with separation of the free acid. On analysis:

Preparation I. 0.1859 gave 0.0699 silver. $Ag = 37.50$.

.. I. 0.2128 „ 0.0800 „ $Ag = 37.59$.

.. II. 0.1316 „ 0.0496 „ $Ag = 37.68$.

Mean $Ag = 37.59$.

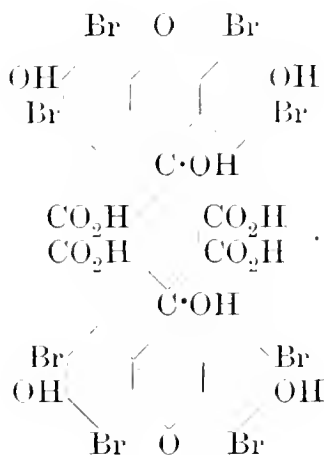
$C_{36}H_{18}O_{16}Ag_4$ requires $Ag = 37.94$ per cent.

The *copper* salt is a greenish-yellow precipitate, turning darker in colour on addition of ammonia.

The *barium* salt is a yellowish-orange powder.

The *cobalt*, *lead*, *ferrous*, *chromium*, and *mercuric* salts are heavy brown powders, the *ferric* salt being dark yellowish-orange.

2 : 2' : 4 : 4' : 5 : 5' : 7 : 7' - Octabromo - 3 : 3' : 6 : 6' : 9 : 9' - hexahydroxy - p-dixanthylbenzenetetracarboxylic Acid (Octabromotetraresorcinol-mellitein), $C_{36}H_{14}O_{16}Br_8$.



This is prepared by suspending the foregoing acid in glacial acetic acid and adding excess of bromine. After allowing to stand 24 hours, the mixture is heated on the water-bath for one hour, allowed to stand overnight, and poured into water. The precipitate of the bromo-compound is separated and thoroughly washed with boiling water, dissolved in a small quantity of alcohol, filtered, and the compound precipitated from its alcoholic solution by the addition of water. It is further purified by fractional precipitation. On analysis:

Preparation	I.	0.3216	gave	0.3621	AgBr.	Br = 47.91.
„	II.	0.2070	„	0.2310	AgBr.	Br = 47.48.
„	III.	0.4951	„	0.5528	AgBr.	Br = 47.51.
						Mean Br = 47.63.

$C_{36}H_{11}O_{16}Br_8$ requires Br = 47.68 per cent.

The compound is a dark reddish-brown, amorphous powder, which on rapid heating commences to decompose at 260° . It dyes silk and wool a brownish-pink. It is insoluble in water, chloroform, benzene, or concentrated hydrochloric acid, and readily soluble in ethyl acetate, phenol, acetone, aniline, or alcohol, which latter gives a blood-red solution having a brown fluorescence, the compound being precipitated on addition of water. It is also soluble in concentrated sulphuric acid, being precipitated on dilution with water, and very soluble in dilute caustic alkalis or ammonia, giving deep blood-red solutions having a brownish-green fluorescence; on acidifying, the compound is precipitated. When obtained in this way from acetic acid, it is dark orange-red, whilst from alcohol it is dark reddish-brown.

The *potassium* and *lithium* salts are dark red powders having a dark red, metallic reflex, and are very soluble in water, giving a blood-red solution.

The *silver* salt, $C_{36}H_6O_{16}Br_8Ag_8$, is a dark red powder with a brownish-violet reflex. It is readily soluble in ammonia: dilute nitric or glacial acetic acids dissolve the salt with separation of the free acid. It is very stable to heat and light. On analysis:

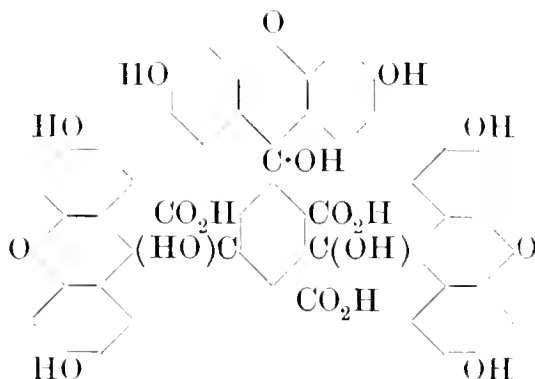
Preparation	I.	0.1767	gave	0.1203	AgBr.	Ag = 39.10.
„	II.	0.1987	„	0.1350	AgBr.	Ag = 39.02.
„	III.	0.1358	„	0.0926	AgBr.	Ag = 39.17.
						Mean Ag = 39.10.

$C_{36}H_6O_{16}Br_8Ag_8$ requires Ag = 39.30 per cent.

The *copper*, *barium*, *cobalt*, *lead*, and *ferrous* salts are precipitated as bright red powders, the copper and barium salts being unaltered by ammonia. The *ferric* and *chromium* salts are deep brownish-red powders.

III. *Trixanthyl Derivatives*. [With WALTER HAMIS GLOVER, Ph.D.]

3 : 3' : 3'' : 6 : 6' : 6'' : 9 : 9' : 9''-Nonahydroxy - sym - trixanthylbenzene-2 : 4 : 6-tricarboxylic Acid (*Hexaresorcinol-mellitein*), $C_{48}H_{30}O_{18}$.



This compound is obtained by heating a mixture of 17 parts of mellitic acid and 33 parts of resorcinol to 160° for eight hours. Condensation rapidly occurs, the fused mass gradually thickening, and becoming solid and almost black in colour. The fusion is extracted with dilute aqueous caustic potash, and the condensation product precipitated with acid and purified by repeated fractional precipitation from its alcoholic solution by the addition of water. On analysis :

I.* 0.1783 gave 0.4219 CO_2 and 0.0550 H_2O . C = 64.53 ; H = 3.42.

II. 0.2103 „ 0.4981 CO_2 „ 0.0658 H_2O . C = 64.60 ; H = 3.47.

III. 0.2100 „ 0.4991 CO_2 „ 0.0657 H_2O . C = 64.81 ; H = 3.47.

Mean C = 64.65 ; H = 3.45.

$C_{48}H_{30}O_{18}$ requires C = 64.42 ; H = 3.35 per cent.

The acid is a yellowish-orange, slightly hygroscopic, amorphous powder, which decomposes, without melting, above 300° . It dyes silk and wool brownish-yellow. It is insoluble in cold water, ether, benzene, chloroform, or ethyl acetate, slightly soluble in phenol or concentrated hydrochloric acid, and readily so in aniline, acetone, or alcohol, giving with the latter a yellow solution having a most intense green fluorescence. It is fairly soluble in glacial acetic acid, from which solution it is precipitated on dilution. With concentrated sulphuric acid it gives a dark red solution, from which the acid is precipitated unaltered on dilution with water.

In dilute caustic alkalis or ammonia it is very soluble, giving a green fluorescence even in extremely dilute solutions. On acidifying these solutions, the compound is precipitated.

The *ammonium* salt is a reddish-yellow powder having a green,

* See footnote on p. 1796.

metallic reflex. The *potassium* and *lithium* salts are dark orange-red powders having a green reflex.

The *silver* salt, $C_{48}H_{27}O_{18}Ag_3$, is a buff-coloured powder, readily soluble in ammonia. Dilute nitric or glacial acetic acids dissolve the salt with separation of the acid. It is fairly stable to heat and very stable to light. On analysis :

Preparation I. 0.3127 gave 0.0793 Ag. $Ag = 25.36$.

„ II. 0.2009 „ 0.0511 Ag. $Ag = 25.43$.

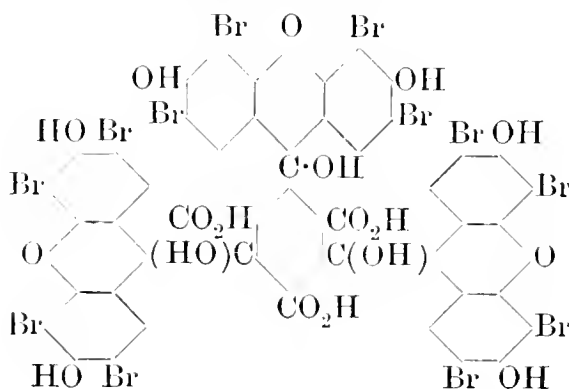
Mean $Ag = 25.40$.

$C_{48}H_{27}O_{18}Ag_3$ requires $Ag = 25.51$ per cent.

The *copper*, *cobalt*, *barium*, *lead*, and *mercuric* salts are precipitated as reddish-orange powders.

The *ferric*, *ferrous*, and *chromium* salts are brown.

2 : 2' : 4 : 4' : 5 : 5' : 7 : 7'-Dodecabromo-3 : 3' : 3'' : 6 : 6' : 6'' : 9 : 9' : 9''-nonahydroxy - sym - trixanthylbenzene - 2 : 4 : 6-tricarboxylic Acid (Dodecabromohexaresorcinol-mellitein), $C_{48}H_{18}O_{18}Br_{12}$.



The foregoing acid is dissolved in glacial acetic acid, excess of bromine added, and the mixture boiled for six hours, allowed to stand overnight, then poured into water. The precipitate is thoroughly washed with boiling water and purified by exhaustive fractional precipitation from its alcoholic solution by the addition of water. On analysis :

Preparation I. 0.3161 gave 0.3892 AgBr. $Br = 52.39$.

„ II. 0.1893 „ 0.2331 AgBr. $Br = 52.39$.

„ III. 0.2912 „ 0.3590 AgBr. $Br = 52.46$.

Mean $Br = 52.41$.

$C_{48}H_{18}O_{18}Br_{12}$ requires $Br = 52.08$ per cent.

The substance is a dark red, amorphous powder, which on rapid heating froths up at 210° . It dyes silk and wool red, with a tinge of violet. It is insoluble in water, benzene, ether, ethyl acetate, or

concentrated hydrochloric acid, slightly soluble in glacial acetic acid or concentrated sulphuric acid; the latter solution is yellow, and on dilution the compound is precipitated unaltered,

It is very soluble in acetone, phenol, or alcohol, giving with the latter a dark red solution having a brown fluorescence; on dilution, the acid is precipitated as a dark red powder. In dilute caustic alkalis or ammonia it is exceedingly soluble, forming dark crimson solutions having a brown fluorescence, and on acidifying the compound is precipitated.

The *potassium* and *lithium* salts are dark red powders, having a dark red, metallic reflex.

The *silver* salt, $C_{48}H_9O_{18}Br_{12}Ag_9$, is a dark violet-red powder, which becomes still darker on heating. It is readily soluble in ammonia: dilute acids dissolve the salt with separation of the acid. On analysis:

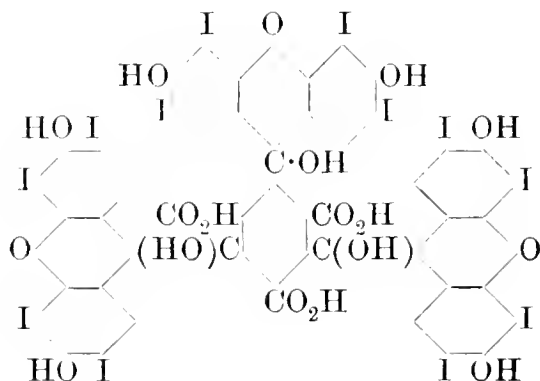
Preparation	I.	0.2568	gave	0.1542	AgBr.	Ag = 34.50.
„	I.	0.2007	„	0.1205	AgBr.	Ag = 34.49.
„	II.	0.1081	„	0.0648	AgBr.	Ag = 34.43.
						Mean Ag = 34.47.

$C_{48}H_9O_{18}Br_{12}Ag_9$ requires Ag = 34.64 per cent.

The *barium*, *chromium*, *cobalt*, *copper*, and *lead* salts are blood-red powders. The barium salt is unaltered by ammonia, but the copper salt becomes reddish-violet.

The *ferric* and *ferrous* salts are brownish-red.

2:2':2'':4:4':4'':5:5':5'':7:7':7'':-Dodecaiodo-3:3':3'':6:6':6'':-9:9':9'':-nonahydroxy-sym-trixanthylbenzene-2:4:6-tricarboxylic Acid (Dodecaiodohexaresorcinol-mellitein), $C_{48}H_{18}O_{18}I_{12}$.



8.9 Parts of nonahydroxy-sym-trixanthylbenzenetricarboxylic acid are dissolved in 40 parts of 50 per cent. aqueous caustic potash and heated to boiling; 60 parts of iodine are dissolved in 15 parts of aqueous caustic potash and added slowly to the hot liquid, the temperature being allowed to rise. When all the iodine solution is added, the

mixture is boiled for ten minutes, then allowed to cool, when the iodo-compound separates. The product is filtered off and purified by repeated fractional precipitation from its solution in caustic potash by the addition of acid. On analysis :

Preparation I. 0.2109 gave 0.2455 AgI. I = 62.91.

„ II. 0.1592 „ 0.1859 AgI. I = 63.11.

Mean I = 63.01.

$C_{48}H_{18}O_{18}I_{12}$ requires I = 63.33 per cent.

The compound is a dark orange-red, amorphous powder, which when rapidly heated loses iodine at 255° , and on further heating decomposes completely without melting. It dyes silk and wool pink. It is insoluble in ether, benzene, chloroform, ethyl acetate, or concentrated hydrochloric acid, slightly soluble in glacial acetic acid or alcohol, giving orange solutions, and fairly so in acetone or phenol, giving deep red solutions. It is very soluble in aniline, slightly so in concentrated sulphuric acid, and readily so in dilute aqueous caustic potash, giving a fine deep red coloured solution, from which the acid is precipitated on acidifying.

The *potassium* and *lithium* salts are very dark red powders, readily soluble in water, giving deep red solutions.

The *silver* salt, $C_{48}H_9O_{18}I_{12}Ag_9$, forms a heavy, deep red precipitate, which dries to a dark violet-red powder having a violet reflex. It is soluble in ammonia : dilute acids dissolve the salt with separation of the acid. It is fairly stable to heat and light. On analysis :

Preparation I. 0.1258 gave 0.0797 AgI. Ag = 29.11.

„ II. 0.1551 „ 0.0983 AgI. Ag = 29.13.

„ III. 0.2119 „ 0.1339 AgI. Ag = 29.03.

Mean Ag = 29.09.

$C_{48}H_9O_{18}I_{12}Ag_9$ requires Ag = 28.85 per cent.

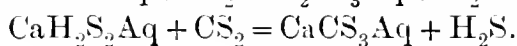
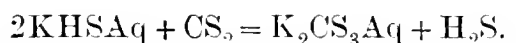
The *copper*, *barium*, *lead*, *cobalt*, *ferrous*, and *chromium* salts are precipitated as heavy, bright red powders, the copper and barium salt being unaltered by ammonia. The *ferric* salt is dull reddish-orange.

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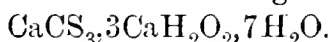
CLXXIV.—*Thiocarbonic Acid and some of its Salts.*

By IDA GUINEVERE O'DONOGHUE, B.Sc., and ZELDA KAHAN, B.Sc.

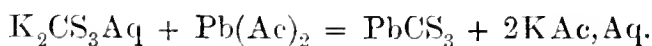
By the interaction of aqueous solutions of hydrosulphides and carbon disulphide, Berzelius (*Trans. Acad. Roy. Stockholm*, 1826, *Ann. Phys. Chem.*, 1826, **6**, 425) obtained unstable solutions of a number of metallic derivatives of thiocarbonic acid which yielded unstable crystalline salts. These on distillation evolved carbon disulphide, and left a residue of sulphide, their constitution being deduced from the method of formation according to the equations :



By the action of hydrochloric or sulphuric acids on the dry salts, a red oil was obtained which rapidly decomposed, and was similar to the one discovered and described by Zeise in 1824, who found it to be equally unstable. In 1862, Berzelius' experiments were repeated by Huseman (*Annalen*, **123**, 67), who also prepared complex salts of the thiocarbonates, isocyanates, &c., which were more stable. Sestini (*Gazzetta*, 1871, **1**, 473), during some experiments on the solubility of carbon disulphide in water, exposed calcium hydroxide, carbon disulphide, and water to sunlight for some time. The mixture reacted slowly, and the red solution gave crystals to which he assigned the formula



Similarly, Walker (*Chem. News*, 1874, **30**, 28) obtained a basic thiocarbonate to which he gave the formula $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 6\text{H}_2\text{O}$. A salt similar to this, but containing $10\text{H}_2\text{O}$, was obtained by Veley (*Trans.*, 1885, **47**, 478), who also repeated Berzelius' and Zeise's experiments with very similar results. Amongst other basic thiocarbonates, he also obtained deliquescent, red crystals which corresponded to the formula $\text{CaH}_2\text{O}_2, \text{CaCS}_3, 7\text{H}_2\text{O}$. It will be seen, therefore, that, although much work has been done on the thiocarbonates, the solid normal salts have been but little investigated, if indeed they have been obtained at all, and owing to their instability their constitution has been inferred merely from their methods of formation, namely :



The experiments to be described below were undertaken at the suggestion of Sir William Ramsay, and had for their aim the formation

of the pure normal thiocarbonates and the elucidation of their constitution. It is extremely difficult to deal quantitatively with the normal salts owing to their instability, but the ratios of their elements have been determined.

Thiocarbonic acid has been prepared in considerable quantities. It has been analysed and its properties investigated, and very nearly pure metallic thiocarbonates have been prepared from it. Their analyses prove the acid to have the constitution H_2CS_3 .

Preparation of Calcium Thiocarbonate in Solution.—This substance was prepared by shaking together calcium hydrosulphide, carbon disulphide, and air-free water in a well-stoppered bottle as nearly full as possible. An orange solution was obtained which always contained polysulphides. Various attempts were made to free the solution from the latter, the most successful being the addition of carbon disulphide and calcium hydroxide in small quantities, and shaking (often for several days), until the solution no longer gave a black precipitate with lead acetate. Such a solution was red and quite stable when kept out of contact with air, but when exposed to the atmosphere it at first slowly deposited red or orange, needle-shaped crystals, then gradually became paler in colour, giving rise to a variety of products, amongst which were identified sulphur, carbonates and sulphides. The solution had a peculiar odour, and with solutions of the salts of the heavy metals yielded characteristic coloured precipitates, which decomposed in air and could not be dried.

By complete evaporation in a vacuum, a crystalline mass was obtained which was only partially soluble in water and was mixed with some white and green substance. The soluble portion consisted of either basic or normal calcium thiocarbonate, since it gave with lead acetate the characteristic bright red lead thiocarbonate. On attempting to obtain crystals again by re-evaporating in a vacuum, there only resulted a mixture of white and green substances.

By evaporating a solution of calcium thiocarbonate to a small bulk in a vacuum, long, red, and sometimes orange, needles were obtained, the colour of which gradually faded in air. They were completely insoluble in water, and became colourless on heating on a platinum foil in a dry test-tube or in water. Although these crystals seem to resemble in some respects those obtained by Berzelius, Sestini, Walker and Veley, analysis shows them to correspond to the formula



	$2\text{CaCS}_3, 5\text{CaH}_2\text{O}_2, 10\text{H}_2\text{O}$		Walker. $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 6\text{H}_2\text{O}$	Veley. $\text{CaCS}_3, \text{CaH}_2\text{O}_2, 7\text{H}_2\text{O}$	Sestini. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 7\text{H}_2\text{O}$
	Found (per cent.).	Calculated (per cent.).	Found (per cent.).	Found (per cent.).	Found (per cent.).
Ca ...	33.57	33.82	29.70	22.99	32.2
S ...	23.34	23.18	23.76	27.77	19.3
C	2.65	2.8	2.96	3.65	2.4
H	3.57	3.38	3.96	—	4.0

By adding alcohol to the red solution and shaking, minute, crystalline, yellow plates were slowly precipitated. When freshly prepared, they were soluble in water, but on standing they gradually turned white, at the same time becoming more and more insoluble. Analysis gave :

Ca = 29.00 ; S = 17.92 ; C = 2.7 ; H = 4.5. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 9\text{H}_2\text{O}$ requires Ca = 30.00 ; S = 18.04 ; C = 2.30 ; H = 4.50 per cent.

Water of crystallisation = 25.5. The above salt containing $9\text{H}_2\text{O}$ requires 30 per cent., or with $7\text{H}_2\text{O}$, 25.4 per cent. Probably the last 2 molecules of water are difficult to remove.

The dry yellow salt was washed with liquid ammonia in order to remove as much water as possible. The substance obtained gave on analysis :

Ca = 23.0 ; S = 36.9. $\text{CaCS}_3, 3\text{Ca}(\text{OH})_2, 3\text{H}_2\text{O}$ requires Ca = 22.6 ; S = 37.7 per cent.

On several occasions, as already mentioned, a green salt was obtained which gave on analysis :

Ca = 32.50 ; S = 21.1 per cent.

Enough of it has never since been prepared pure to enable the determination of carbon and hydrogen to be made. This salt has also been found repeatedly in bottles containing a solution of calcium thiocarbonate.

General Methods of Analysis.—The ordinary Carius method for determining sulphur was found to be the most satisfactory, the metal being estimated in the same solution. In this way, the ratio of metal to sulphur was obtained in those cases in which the salt could not be weighed. A large excess of nitric acid, a high temperature, and prolonged heating were required to decompose the oily drops which were often formed and which resembled carbon disulphide, or possibly thiocarbonic acid, in appearance. In the determination of carbon and hydrogen, the substance was well mixed with freshly-fused potassium dichromate, lead chromate replacing copper oxide in the combustion tube.

It is evident that calcium thiocarbonate is able to form a large number of basic salts, the composition of which depends largely on the

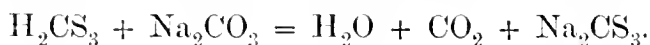
exact conditions of the experiment. The following have been obtained up to the present :

1. $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 6\text{H}_2\text{O}$ (Walker).
2. $\text{CaCS}_3, \text{CaH}_2\text{O}_2, 7\text{H}_2\text{O}$ (Veley).
3. $\text{CaCS}_3, 2\text{CaH}_2\text{O}_2, 10\text{H}_2\text{O}$ (Veley).
4. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 7\text{H}_2\text{O}$ (Sestini).
5. $2\text{CaCS}_3, 5\text{CaH}_2\text{O}_2, 10\text{H}_2\text{O}$ (red needles).
6. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 9\text{H}_2\text{O}$ (yellow plates).
7. $\text{CaCS}_3, 3\text{CaH}_2\text{O}_2, 3\text{H}_2\text{O}$.
8. Green crystals containing $\text{Ca} = 32.5$ and $\text{S} = 21.1$ per cent.

Thiocarbonic Acid.—The above-mentioned oil could scarcely be detected by dropping acid on to the solid salts, but if a test-tube shaped vessel is partially filled with concentrated hydrochloric acid, and a solution of calcium thiocarbonate slowly dropped in, small drops of oil speedily appear and fall to the bottom. It was found best, however, to cool both solutions previously in a freezing mixture, and to allow the vessel to stand for some time after all the calcium thiocarbonate solution had been added. After an hour or two, the liquid was decanted, the last drops being separated with a separating funnel. The oil was sometimes washed rapidly with ice-cold water, but usually it was found best to dispense with this operation. It was then placed in a small flask surrounded by a freezing mixture, calcium chloride added, and the flask attached to a good pump until bubbles no longer appeared to arise from the oil. In this way hydrochloric acid and water were removed, and the oil was finally dried over phosphorus pentoxide.

The free acid is red in colour and appears darker in some preparations than in others. It has a peculiar, pungent odour, and is soluble in alcohol, giving a yellow solution which decomposes rapidly with deposition of sulphur and formation of carbon disulphide and hydrogen sulphide. It is also soluble in liquid ammonia, turpentine, toluene, ether, or chloroform, in all of which solvents it very soon decomposes, but is most stable in the two latter. In liquid air or solid carbon dioxide it forms a pink solid which melts again to a red liquid on removing the refrigerator. The acid is insoluble in water, but is at once decomposed by it, with evolution of hydrogen sulphide and formation of carbon disulphide and sulphur. This also occurs in a solution of common salt. It is much more stable towards strong acids, especially hydrochloric acid, under which it can be kept for several days if cool. The colour, however, gradually fades, and finally only carbon disulphide is left. In air, it gradually evaporates, often leaving a brownish-black residue consisting largely of sulphur. Sometimes it has been kept for a few days in a loosely-stoppered flask without any considerable loss. The oil dissolves flowers of sulphur readily with

a slight darkening in colour, and it is possible, therefore, that the colour of the oil is due to dissolved sulphur. It does not burn on water like carbon disulphide. Calcium and sodium carbonates produce effervescence with production of the corresponding thiocarbonate,



Sodium and potassium act on the dry oil or on its ethereal solution. Potassium decomposes it very violently, giving an immediate yellow, crystalline precipitate of potassium thiocarbonate, whilst in the former case sodium thiocarbonate gradually separates. Hydrogen sulphide and probably hydrogen are evolved in both cases. Magnesium powder has apparently little action on the oil, and on trituration with mercury a red solid is obtained.

The oil, purified as described above, was analysed :

S = (I) 90.16; (II) 89.41. H_2CS_3 requires S = 87.3, H_2CS_4 requires S = 90.14 per cent.

The salts formed by the oil, however, do not seem to correspond to derivatives of H_2CS_4 . It is therefore more probable that it consists of H_2CS_3 , containing sulphur in solution. An attempt was therefore made to distil the acid under diminished pressure from a flask connected with two receivers surrounded by liquid air.

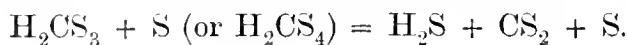
The first distillate was freed from hydrogen sulphide by partly withdrawing the liquid air and allowing the gas which escaped to condense in the second vessel. After standing in a mixture of ice and salt for a quarter of an hour, there was no longer an odour of hydrogen sulphide, and an analysis gave :

S = 84.0. CS_2 requires S = 84.2 per cent.

The distillate had all the properties of pure carbon disulphide.

The second receiver contained hydrogen sulphide and only a few drops of oil. In the distilling flask there remained a brownish-red solid which was chiefly sulphur. The temperature of distillation was 20—30°.

The acid had thus decomposed in accordance with the equation :



At the ordinary pressure, the oil distils at about 50° with decomposition.

With salts of the heavy metals the oil gives the corresponding thiocarbonates. The precipitations were usually carried out at the temperature of solid carbon dioxide. The oil was used either alone or in alcoholic or ethereal solution, and the salt of the weakest acid obtainable was usually employed. The salts thus prepared were

identical with those obtained from a solution of calcium thiocarbonate, but were purer and darkened more slowly.

The *lead* salt, PbCS_3 , is precipitated as a bright red, amorphous solid which, when pure, only darkens slowly in air. This change, according to the equation $\text{PbCS}_3 = \text{PbS} + \text{CS}_2$, takes place more rapidly in an evacuated desiccator, and is quantitative when the salt is distilled in hydrogen.

On analysis :

$\text{PbS} = 75.5$. PbCS_3 requires $\text{PbS} = 75.8$ per cent.

The distillation was carried on in a current of hydrogen. The freshly-prepared salt was placed in a small flask and heated by means of an oil-bath in a current of hydrogen. The moisture was absorbed in a tube containing sulphuric acid, and the carbon disulphide in a vessel immersed in liquid air, lead sulphide being left in the receiver.

In general, the lead salt turned black in about half an hour, but occasionally a very small quantity adhering to a glass rod or at the bottom of a beaker would retain its colour for days, and sometimes weeks.

Cadmium salt.—This was obtained as a deep yellow precipitate, which on shaking changed to a reddish-yellow and then to a reddish-brown substance. The latter was identified as cadmium sulphide.

On analysis :

$\text{Cd} : \text{S} = 1.10$. CdCS_3 requires a ratio of $\text{Cd} : \text{S} = 1.16$; CdCS_4 a ratio of $\text{Cd} : \text{S} = 0.87$.

After drying over calcium chloride :

$\text{Cd} : \text{S} = 3.03$. CdS requires a ratio of $\text{Cd} : \text{S} = 3.50$.

Zinc salt.—This is a pale yellow, insoluble, crystalline powder. When freshly prepared, it corresponds to ZnCS_3 , but rapidly decomposes with formation of zinc sulphide.

Sodium salt, Na_2CS_3 .—This was precipitated by adding a dry, freshly-prepared solution of sodium ethoxide to the oil. A yellow, crystalline precipitate gradually formed, which was washed with cold alcohol. It is deliquescent and very easily soluble in water, giving a yellow solution, which, with lead acetate, gives the pure characteristic lead thiocarbonate with no trace of black colour.

On analysis :

$\text{Na} : \text{S} = 0.48$. Na_2CS_3 requires the ratio $\text{Na} : \text{S} = 0.479$.

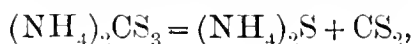
On drying, the salt decomposed and a mixture of several substances was formed.

Potassium salt, K_2CS_3 .—This was precipitated by adding alcoholic

potassium hydroxide to the oil. It resembles the sodium salt, being yellow and crystalline, but is more deliquescent. The aqueous solution also gave a precipitate of pure lead thiocarbonate with lead acetate. The salt is very soluble in liquid ammonia, and when washed with small quantities of this solvent the colour seemed to become lighter, but darkened again on drying. On evaporating the ammoniacal solution, pure potassium thiocarbonate was obtained.

Ammonium salt.—(1) Liquid ammonia and alcoholic thiocarbonic acid, cooled in liquid ammonia, gave a yellowish-pink solution, which, on spontaneous evaporation, yielded a yellow precipitate which soon turned pink. When allowed to remain overnight on a porcelain plate in a desiccator, it decomposed. White, micaceous crystals were obtained on standing for a short time, and were identified as ammonium sulphide. The ammoniacal mother liquor also yielded white needles of sulphur, probably from excess of sulphur in the oil. The yellowish-pink salt was not analysed, but gave pure lead thiocarbonate with lead acetate, and was most probably ammonium thiocarbonate.

Its decomposition is represented by the equations :



and



(2) By shaking dry redistilled carbon disulphide with a saturated solution of ammonia in alcohol, a pale yellow, crystalline precipitate was obtained in about five minutes. It has a peculiar odour, rather different from that of the thiocarbonates. Lead acetate does not give a characteristic precipitate, nor could thiocarbonic acid be obtained from it. When heated, it melts and partially sublimes, at the same time decomposing and evolving hydrogen sulphide and ammonia. It decomposes very gradually in air, becoming moist in appearance. Analysis showed that it is not ammonium thiocarbonate, but its investigation is not yet completed.

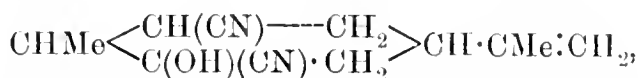
In conclusion, we wish to express our thanks to Sir William Ramsay for the encouragement and help he has given us during the progress of this work.

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CLXXV.—*Derivatives of Cyanodihydrocarvone and Cyanocarvomenthone.*

By ARTHUR LAPWORTH.

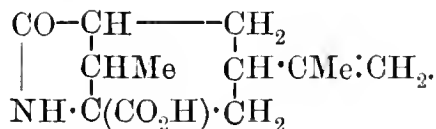
CYANODIHYDROCARVONE, the product obtained when carvone is acted on by potassium cyanide (Trans., 1906, 89, 949), is very readily converted into its *cyanohydrin*. The new substance, which has the formula



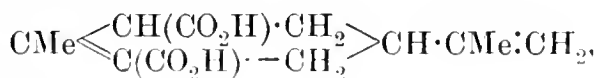
is unstable, being easily resolved by heat or by the action of alkalis, so that on attempting to crystallise it from warm solvents an impure product containing regenerated cyanodihydrocarvone is obtained. In presence of small quantities of mineral acids, however, it becomes much more stable, and can be heated at temperatures considerably above its melting point without appreciable change.

The conversion of the carbonyl group of cyanodihydrocarvone into $>\text{C} \begin{array}{c} \text{OH} \\ \text{CN} \end{array}$ results in the production of a fourth asymmetric carbon atom within the molecule, so that sixteen active modifications of the cyanohydrin are possible, eight being derived from *d*-carvone. A careful search was made in the hope of detecting the presence of more than one isomeride in the crude substance but without success, all the fractions appearing to be identical in properties. The conversion of the ketonitrile into its cyanohydrin being a reversible process under the conditions employed, the separation of only one of the solid modifications is not altogether surprising, as they are thus mutually intraconvertible, a type of labile dynamic isomerism being exhibited.

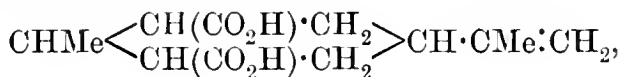
The cyanohydrin, when hydrolysed by means of cold mineral acids, is converted into a mixture of isomeric nitrogenous acids which present basic as well as acidic characters. These substances are doubtless internal anhydrides of aminodicarboxylic acids analogous in constitution to mesitylic acid. Their structure is thus probably



When heated either with strong acids or alkalis these compounds lose their nitrogen as ammonia, and are converted into a dicarboxylic acid which has the constitution



which may be regarded as derived from the original cyanohydrin by the conversion of the cyano- into carbonyl-groups and the simultaneous elimination of the elements of water with formation of an ethylenic carbon linking. The new compound, *2-methyl-5-iso-propenyl- Δ^2 -tetrahydroisophthalic acid*, has all the characters of an acid with the above structure, and, in accordance with its representation as an acid having only one double linking situated in the $\alpha\beta$ -position with regard to a carboxyl group, it unites with only two atomic proportions of hydrogen when reduced with sodium amalgam. The product, *2-methyl-5-iso-propenylhexahydroisophthalic acid*,



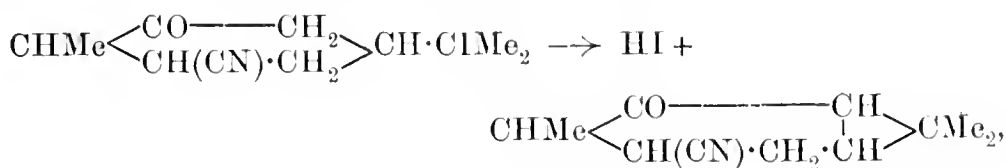
behaves as an unsaturated compound towards bromine and potassium permanganate.

The formula of the tetrahydro-acid, containing, as it does, two asymmetric carbon atoms, one of these being that present in the original *d*-carvone from which the compound was prepared, indicates that two modifications of the acid might be obtained from the dextro-ketone. The substance, prepared by the above method, however, was homogeneous, but on reduction to the hexahydro-acid yielded a mixture.

In connexion with the constitution of the hexahydro-acid, it is interesting to notice that the molecule is, for the first time, symmetrical about the horizontal line bisecting the ring plane in the above formula. The optical activity due to the apical carbon atom, which was the only asymmetric one in the original carvone molecule, no longer exists. Meanwhile, however, two other atoms have become asymmetric, namely, those to which the carboxyl groups are attached, and these are equivalent in the same sense as are the asymmetric atoms in tartaric acid, so that internally compensated as well as active and racemic forms may exist. Taking into consideration the *cis-trans*-isomerism due to the presence of the $\text{:C} \begin{array}{c} \text{H} \\ < \\ \text{CH}_3 \end{array}$ and $\text{:C} \begin{array}{c} \text{H} \\ < \\ \text{C}_3\text{H}_5 \end{array}$ groups in the ring, the existence of four *meso*-, two *dextro*-, two *laevo*-, and two racemic forms may be predicted, all of which are theoretically to be obtained from either of the enantiomorphous forms of carvone. The case is therefore one of unusual interest, but unfortunately, owing to the small quantity of material which was available, only one of the four possible active forms was isolated from the mixture.

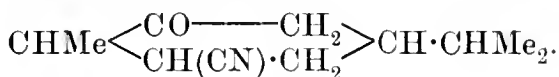
In the hope finally of obtaining cyanocarone and cyanocarvo-menthone, the properties of the hydrogen halide addition products of cyanodihydrocarvone were studied. Of the three halogen derivatives, which are all well characterised solids, the hydriodide is by far the

most reactive. It was expected that, by the action of alcoholic alkalis, it would yield cyanocarvone as follows :



but although the product when boiled with excess of alkali gave the colour test for eucarvone, only monocyclic compounds could be isolated.

More success was met with in the attempt to convert the halogen compounds into cyanocarvomenthone,

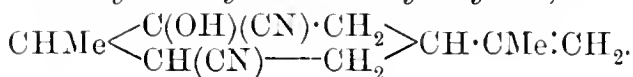


By the action of zinc dust on a cold alcoholic solution of the hydrobromide, or, better, the hydriodide, a mixture of cyanodihydrocarvone and cyanocarvomenthone is obtained; the hydrochloride is not affected when subjected to this treatment. The cyanocarvomenthone was at last isolated from the mixture by shaking a solution of the material in benzene with cold potassium permanganate, which converts the unsaturated compound into acids easily soluble in alkali, while the reduced nitrile is not affected by it.

Cyanocarvomenthone resembles cyanodihydrocarvone very closely except in its character as an unsaturated compound. Like the latter substance, it could be isolated in one form only, the isomerides being apparently intraconvertible in presence of alkalis. When it is heated with alcoholic potassium hydroxide, it is converted into carvotanacetone (Δ^6 -menthenone⁽²⁾), $\text{CMe} \begin{array}{c} \text{CO} \text{---} \text{CH}_2 \\ \text{CH} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CHMe}_2$, hydrogen cyanide being eliminated, and it is probable that this method represents the most satisfactory method of preparing this ketone from carvone, as by the usual method (Harries, *Ber.*, 1901, **34**, 1024) the separation of the ketone from carvone is exceedingly tedious.

By the action of mineral acids on cyanocarvomenthone a mixture of isomeric cyanocarvomenthonicarboxylic acids is obtained, stereoisomeric change having occurred as in the similar case of the cyanodihydrocarvone (Trans., 1906, **89**, 948). Only one of the isomerides was isolated in a quite pure condition, and this had the character of a saturated ketonic acid, yielding solid derivatives with semicarbazide and hydroxylamine. When distilled with soda-lime it gave a small quantity of a saturated ketone, possibly carvomenthone.

EXPERIMENTAL.

*Addition of Hydrogen Cyanide to Cyanodihydrocarvone.**Cyanodihydrocarvonecyanohydrin,*

This cyanohydrin may be obtained in one operation from carvone (compare Trans., 1906, 89, 949), but it is better to prepare it from purified cyanodihydrocarvone, and the conversion may be brought about by allowing the ketonitrile to remain for some hours in a closed vessel with an aqueous solution of potassium cyanide, to which slightly more than one molecular proportion of sodium bicarbonate has been added. The transparent crystals of the nitrile rapidly grow opaque as they become coated with the minute, slender needles of the cyanohydrin. When the reaction is complete, excess of mineral acid may be added, and the solid matter at once removed by filtration.

The use of soluble bicarbonates for liberating hydrocyanic acid in such cases is to be recommended, especially in dealing with small quantities of material, because even a very large excess of these salts does not inhibit the addition process, but with large quantities it is equally effectual in most cases to dissolve the ketonic compound in alcohol and to add an aqueous solution of potassium cyanide (1 mol.), and then acetic acid (1 mol.) by means of a thistle-funnel provided with a fine orifice. At the end of fifteen minutes excess of hydrochloric acid is added, the solution diluted largely with water, and the precipitated solid collected and washed on a filter.

The product should be dried and crystallised by dissolving it in cold ethyl acetate and adding light petroleum rapidly until separation of crystals commences. On analysis :

0·1570 gave 0·4075 CO₂ and 0·1103 H₂O. C = 70·8 ; H = 7·7.

C₁₂H₁₆ON₂ requires C = 70·6 ; H = 7·8 per cent.

The compound is insoluble in water, somewhat sparingly soluble in light petroleum and readily so in benzene, chloroform, alcohol esters, or acetic acid. It separates from a mixture of ethyl acetate and light petroleum in long, very slender needles melting between 104° and 108° according to the rate of heating. The crystals are very feebly doubly refracting and show straight extinction in polarised light.

The substance, except in presence of excess of mineral acid, is very unstable and loses hydrogen cyanide if recrystallised from hot solvents or if heated alone above 80°, and this accounts for its indefinite melting point.

0·4010 gram dissolved and made up to 25 c.c. with absolute alcohol

was examined in a 2-dem. tube at 18° ; the observed rotation was $+0.367^\circ$, whence $[\alpha]_D +11.5^\circ$.

Attempts to replace the hydroxyl group by chlorine or bromine or to acetylate the substance were unsuccessful.

Hydrolysis of cyanodihydrocarvonecyanohydrin.—It was found that the most convenient method of hydrolysing the nitrile was to heat it with fuming hydrochloric acid, a small quantity of acetic acid being added to promote the reaction by raising the solubility of the solid.

At the end of some hours, when the solution is complete, the whole is filtered from a small quantity of insoluble matter and evaporated to a small bulk. On adding water to the residue, a nearly colourless, gummy mass is precipitated, which becomes semi-crystalline when triturated with strong hydrochloric acid. The material may be drained on porous porcelain, and crystallised from a mixture of benzene and light petroleum.

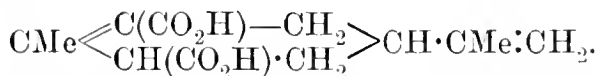
This product, although it forms crystals of considerable size, is doubtless a mixture, as different fractions varied considerably in rotatory power ($[\alpha]_D +4.0$ to $+7.0$), and the melting point varied between 97 and 107° . The whole dissolves readily in most of the usual organic media with the exception of light petroleum, but tends to separate, in most cases, as an oil. It is sparingly soluble in water, but dissolves freely in strong mineral acids and in sodium carbonate solution. On analysis:

0.2314 gave 0.5449 CO_2 and 0.1610 H_2O . $\text{C} = 64.3$. $\text{H} = 7.7$.

0.3138 „ 16.65 c.c. moist nitrogen at 15° and 767 mm. $\text{N} = 6.5$.

$\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C} = 64.6$; $\text{H} = 7.6$; $\text{N} = 6.3$ per cent.

The compound is slowly hydrolysed either by acids or alkalis, yielding
2-methyl-5-isopropenyl- Δ^2 -tetrahydroisophthalic acid,



This is most easily prepared in quantity by the direct hydrolysis of cyanodihydrocarvone with hydrochloric acid. The cyano-compound is placed in a flask covered with about ten times its weight of hydrochloric acid and heated for several days on the water-bath; the compound first melts and slowly dissolves, forming a clear solution which after prolonged heating slowly deposits a microcrystalline powder, and when this no longer increases in amount it is removed by filtration. A further quantity of the acid may be obtained by evaporating the mother liquid to dryness, dissolving the residue in a large excess of a 35 per cent. aqueous potassium hydroxide solution, and heating until ammonia ceases to be evolved, a process which occupies some six hours. On diluting the resulting liquid and acidifying it

with hydrochloric acid, the product is obtained in pulverulent form.

For the purification of the acid, hot, anhydrous formic acid was found to be the best crystallising medium. A specimen thus treated was dried and analysed :

0.1504 gave 0.3557 CO_2 and 0.0950 H_2O . $\text{C} = 64.5$; $\text{H} = 7.0$.

$\text{C}_{12}\text{H}_{16}\text{O}_4$ requires $\text{C} = 64.3$; $\text{H} = 7.1$.

For the determination of its equivalent, 0.3262 was titrated with $N/10$ sodium hydroxide, using phenolphthalein as indicator ; 28.8 c.c. of the alkali were necessary for neutralisation, whence the equivalent of the acid was 114, that calculated for a dibasic acid of the formula $\text{C}_{12}\text{H}_{16}\text{O}_4$ being 112.

The compound is almost insoluble in benzene, petroleum, chloroform, or water, dissolves sparingly in ethyl acetate or acetone, more readily in formic or acetic acid, and is readily soluble in absolute alcohol, hot quinoline, or dimethylaniline. It sublimes at high temperatures and melts at $281-282^\circ$.

The crystals from hot formic acid are very small, flat-plates or needles, the crystallographic character of which is not easily determined. After fusion between glass slips, the substance sets rapidly to masses of rhomboidal plates of considerable size, and through some of these, viewed in convergent polarised light, one axis of a wide-angled interference figure may be seen emerging nearly perpendicularly.

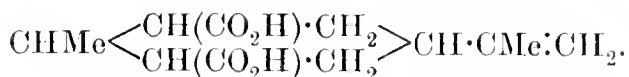
0.3995 gram dissolved and made up to 25 c.c. with absolute alcohol was examined in a 2-dem. tube at 19.5° . A mean rotation of -5.523° was observed, whence $[\alpha]_D - 172.8$.

The substance has the character of an unsaturated acid, and its solution in ice-cold sodium carbonate instantly decolorises a solution of potassium permanganate, although its action on bromine water is very slow. It unites readily with hydrogen iodide or bromide, yielding crystalline compounds which are somewhat unstable, but which appear to contain only one molecular proportion of hydrogen halide ; these are at once decomposed by cold alkalis, yielding the original unsaturated acid.

An anhydride may be obtained from the acid by the prolonged action of acetyl chloride. On evaporating the excess of the reagent under diminished pressure at 100° and leaving the residue for some days over potassium hydroxide, a compound is obtained which is readily soluble in benzene or chloroform, and is precipitated from the resulting solution in an apparently amorphous condition. The substance obtained in this way dissolves only very slowly in cold aqueous sodium carbonate, the resulting solution yielding the dicarboxylic acid on acidification. As it was not obtained perfectly pure, it was not analysed by the

combustion method, but 0.3226 gram was warmed with water for some hours and the product titrated with *N*/10 alkali; 0.1280 gram of NaOH was required for neutralisation; whilst 0.1252 gram was the weight calculated on the assumption that the substance was the anhydride $C_{12}H_{14}O_3$.

Reduction of 2-Methyl-5-isopropenyl- Δ^2 -tetrahydroisophthalic Acid.
2-Methyl-5-isopropenylhexahydroisophthalic Acid.



For the reduction of the foregoing unsaturated acid, a solution in the requisite quantity of 10 per cent. sodium carbonate was placed in a shallow porcelain dish and allowed to remain in the cold with a considerable excess of 2 per cent. sodium amalgam while a slow stream of carbon dioxide was led into the liquid. At the end of two days the mercury was removed and the aqueous liquor acidified with hydrochloric acid, the precipitate formed being removed by filtration, washed with water, dried and extracted with warm anhydrous formic acid, in which the larger proportion of the original acid did not dissolve. By fractional crystallisation of the dissolved material, first from formic acid and finally from methyl alcohol, one of the reduction products was obtained in a pure form. On analysis:

0.2012 gave 0.4692 CO_2 and 0.1412 H_2O . $C = 63.6$; $H = 7.8$.

$C_{12}H_{18}O_4$ requires $C = 63.8$; $H = 8.0$ per cent.

0.1605 gram of the acid required 14.15 c.c. *N*/10 NaOH for complete neutralisation, whence the equivalent was 113, exactly the number required for a dibasic acid, $C_{12}H_{18}O_4$.

For the determination of its optical activity, 0.2326 gram was dissolved and made up to 25 c.c. with absolute alcohol at 17°. The solution in a 2-dm. tube had a mean rotation -0.31° , whence $[\alpha]_D - 16.6$.

The acid dissolved very sparingly in water, benzene, or chloroform, somewhat readily in hot ethyl acetate or formic acid, and is readily soluble in methyl or ethyl alcohol. It separates from methyl alcohol in crystals which melt at 204—205°.

The crystals are flat needles, through the large faces of which one axis of a wide angled biaxial interference figure emerges nearly perpendicularly, and in which the double refraction is strong and negative in sign.

On cooling, the fused substance solidifies rapidly from a centre to masses of needles identical in character with those obtained from solution.

The compound has all the properties of an unsaturated acid. In solution in acetic acid, it absorbs bromine somewhat rapidly, and when a solution of potassium permanganate is added to an ice-cold solution of the sodium salt its colour is instantaneously discharged.

The acid appears to form an anhydride when it is heated with acetyl chloride, as the product is entirely soluble in benzene, but owing to the small quantity of the acid which was available attempts to prepare this derivative in a pure form were not successful.

Addition Products of Cyanodihydrocarvone with Hydrogen Halides.

The *hydrochloride* $\text{CHMe} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CH}(\text{CN}) \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CClMe}_2$ is formed in considerable quantity when cyanodihydrocarvone is shaken with an aqueous solution of hydrogen chloride (saturated at 0°). The nitrile dissolves somewhat rapidly at first and in a short time, if the liquid is kept cold, the hydrochloride separates in a crystalline form. This process, however, is liable to lead to an impure product, and it is more satisfactory to pass hydrogen chloride into a strong solution of the nitrile in glacial acetic acid until it is no longer absorbed, allowing the whole to remain for twenty-four hours and then pouring into water. The solid material which separates may be crystallised from warm dilute alcohol. On analysis:

0.3233 gave 0.2177 AgCl. $\text{Cl} = 16.5$.

$\text{C}_{11}\text{H}_{16}\text{ONCl}$ requires $\text{Cl} = 16.6$ per cent.

It is sparingly soluble in hot light petroleum, more readily so in hot ether or cold alcohol, and dissolves freely in hot alcohol and in ethyl acetate. It separates from alcohol in small prisms or flattened needles melting at $64\text{--}65^\circ$.

The crystals show straight extinction in polarised light; examined in convergent polarised light, some crystals show a biaxial interference figure of small axial angle. The double refraction is positive in sign and fairly strong.

0.3996 gram dissolved and made up to 25 c.c. with absolute alcohol and examined in a 2-dem. tube at 18° gave a mean rotation of 0.810° , whence $[\alpha]_D + 25.3$.

The hydrochloride is somewhat unstable, and is decomposed in the cold if alkalis or solutions of alkali carbonates are added to its alcoholic solution. It is also decomposed when heated with water at a temperature above its melting point. It is less easily reduced than the hydrobromide. The corresponding *hydrobromide*, $\text{C}_{11}\text{H}_{16}\text{ONBr}$, is most easily prepared by dissolving cyanodihydrocarvone in about five times its own weight of a cold saturated solution

of hydrogen bromide in glacial acetic acid. If, at the end of twenty-four hours, the whole is poured into water, the addition product is obtained in a nearly pure condition and may be crystallised from alcohol. On analysis :

0.2784 gave 0.2002 AgBr. Br = 30.6.

$C_{11}H_{16}ONBr$ requires Br = 31.0 per cent.

In general character and in its solubility in organic media, this compound closely resembles the hydrochloride, but it appears to be somewhat less stable towards alkalis and is less easy to obtain in large crystals. The crystallographic description of the preceding compound applies equally well to this. It melts at 82—83°.

The *hydriodide*, $C_{11}H_{16}ONI$, was prepared in considerable quantities by the following method. An aqueous solution of hydrogen iodide, saturated at 20°, was placed in a mortar and a small quantity of cyanodihydrocarvone was introduced, while the whole was rapidly stirred with the pestle; when solution was complete a further quantity of the nitrile was added and the process was continued until fine needles of the hydriodide began to separate. In a few minutes the whole usually set to a semi-solid mass, and this was drained, first on a filter with the aid of a pump and finally on porous earthenware. The dried product was crystallised from alcohol. On analysis :

0.2993 gave 0.2296 AgI. I = 40.0.

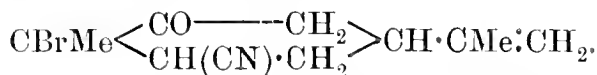
$C_{11}H_{16}ONI$ requires I = 40.2 per cent.

This substance is more readily soluble in organic media than the two preceding compounds. It was always obtained in slender needles having straight extinction. Unless very carefully purified it rapidly becomes deep brown, especially when exposed to light. It melts at 81—82°.

In the hope of obtaining a cyanocarone by the same method as was used by Baeyer, in preparing carone from dihydrocarvone hydrobromide, experiments on the hydrobromide and hydriodide of cyanodihydrocarvone were made. When dissolved in alcohol and mixed with a cold solution of potassium hydroxide in methyl alcohol, they rapidly lost hydrogen halide, as was evidenced by the copious deposition of potassium salt whilst little or no hydrogen cyanide was eliminated. In all the experiments made the product was a somewhat mobile oil, which when boiled with potassium hydroxide dissolved in methyl alcohol, lost hydrogen cyanide, and gave a beautiful blue solution so that derivatives of carone or eucarvone appear to have been formed. Nevertheless no new compound of unquestionable purity could be isolated and the supposed cyanocarone, when hydrolysed with

mineral acids, gave only mixtures of the isomeric dihydrocarvone-carboxylic acids.

Action of Bromine on Cyanodihydrocarvonehydrobromide. Formation of Monobromocyanodihydrocarvone,



In order to prepare a substitution derivative of cyanodihydrocarvone, the hydrobromide of the latter was dissolved in glacial acetic acid and saturated with hydrogen bromide, which served the purpose, not only of ensuring the stability of the hydrobromide and thus preventing attack by the bromine in the *isopropenyl* group, but also of accelerating the substituting action of the halogen (compare *Trans.*, 1904, 85, 31, *et seq.*). To the solution was then added one molecular proportion of bromine, the whole being allowed to remain until the colour of the halogen disappeared, and then poured into water. The separated oil rapidly solidified when washed and the solid was repeatedly crystallised from alcohol.

0.2865 gave 0.2107 AgBr. Br = 31.3.

$\text{C}_{11}\text{H}_{14}\text{ONBr}$ requires Br = 31.2 per cent.

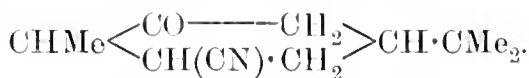
The analysis indicated that only one bromine atom was present, and, as it was suspected that the hydrogen bromide had been lost during recrystallisation, experiments were made to test this point. It was found that the crude product contained nearly two atomic proportions of bromine and that if it was boiled with acetic acid, hydrogen bromide was evolved and the same product as before finally obtained.

The bromo-compound was nearly insoluble in light petroleum, but dissolved somewhat freely in most of the other organic media. It crystallises from alcohol in glistening needles which darken slightly at 170° and melt and decompose at 177°.

Like the dibromides already described, it is rapidly dissolved by strong alkalis in presence of a little alcohol, hydrogen bromide being lost, and on diluting and acidifying, a colourless liquid acid is precipitated which has not yet been closely examined. When it is boiled with alkalis, ammonia is evolved and no cyanide is formed; on acidifying the resulting solution, the acid obtained is still liquid and nearly colourless.

The acid products obtained from the three preceding compounds will be examined in detail later.

Reduction of Cyano dihydrocarvonehydrobromide to Cyanocarvomenthone,



The crude product obtained by the action of hydrogen bromide on cyanodihydrocarvone was washed with water, dissolved in about ten times its weight of 95 per cent. methyl alcohol, and zinc dust was added in small quantities at a time, while the temperature was kept at about 0°. When no further action was perceptible a large excess of zinc was added, the whole transferred to a stoppered bottle and shaken for several days, when the insoluble matter was removed by filtration and washed with alcohol. The united alcoholic solutions were evaporated to a small bulk, diluted with water, and extracted with benzene.

As it was found in a previous experiment that the larger proportion of the product consisted of cyanodihydrocarvone regenerated by the mere removal of hydrogen bromide from the addition compound, the benzene extract was washed repeatedly with water and then shaken with an ice-cold solution of potassium permanganate until the latter ceased to be reduced, the precipitated manganese dioxide being dissolved by means of a stream of sulphur dioxide and the benzene solution then removed, dried, and allowed to evaporate spontaneously.

The material thus prepared was a mixture of two substances, one of which had the properties of an amide and was not closely examined; the other proved to be cyanocarvomenthone, and was separated from the former by extraction in a Soxhlet apparatus with carbon disulphide, in which the amide was not appreciably soluble.

The cyano-compound obtained in this way was crystallised from dilute alcohol, dried, and analysed :

0.2238 gave 0.6052 CO₂ and 0.1951 H₂O. C = 73.7 ; H = 9.7.

C₁₁H₁₇ON requires C = 73.7 ; H = 9.5 per cent.

Cyanocarvomenthone closely resembles the original cyanodihydrocarvone in appearance, but is distinctly more readily soluble in benzene, chloroform, and alcohol. It crystallises from alcohol in flat needles melting at 83—84°.

It is easily distinguished from cyanodihydrocarvone by shaking a few milligrams in a test-tube with a little dilute potassium permanganate solution, when the solution retains its colour for a very long time, whilst the unsaturated nitrile discharges the tint in a few seconds.

The *oxime* was prepared by warming the nitrile in alcoholic solution with free hydroxylamine. After crystallisation from alcohol, it was obtained in flat plates closely resembling the oxime of cyanodihydro-

carvone in appearance and solubility in organic media, but it melted at 156—157°. When the two oximes were mixed in equal proportions the whole fused at 150—151°.

It was very easily hydrolysed by warm dilute mineral acids into cyanocarvomenthone and hydroxylamine.

When the nitrile is heated with strong alcoholic potassium hydroxide, hydrogen cyanide is eliminated, and an odour of peppermint and caraways becomes perceptible. In order to isolate the volatile product of this reaction, a few grams of the nitrile were heated for half an hour with an excess of a solution of potassium hydroxide containing suspended, freshly precipitated ferrous hydroxide; the alcohol was then removed by distillation and the residue distilled in a current of steam. The distillate was extracted with ether, and this on evaporation gave a small quantity of an oil which boiled at 221—222° and gave the following results on analysis :

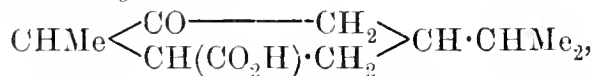
0.1898 gave 0.5470 CO₂ and 0.1842 H₂O. C = 78.5 ; H = 10.7.

C₁₀H₁₆O requires C = 78.8 ; H = 10.5 per cent.

The compound was unsaturated and, when warmed with a dilute alcoholic solution of potassium cyanide, was reconverted almost quantitatively into cyanocarvomenthone. The substance was therefore

carvotanacetone, $\text{CMe} \begin{smallmatrix} \text{CO-CH}_2 \\ \text{CH} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CMe}_2$.

Carvomenthonecarboxylic acid,



was obtained by heating the nitrile for several days with concentrated hydrochloric acid and working up the product in the manner adopted in preparing dihydrocarvonecarboxylic acid. The acid was purified by repeated crystallisation from boiling carbon tetrachloride. On analysis :

0.2383 gave 0.5828 CO₂ and 0.1964 H₂O. C = 66.7 ; H = 9.1.

C₁₁H₁₈O₃ requires C = 66.6 ; H = 9.1 per cent.

0.1725 gram required 8.85 c.c. of N/10 sodium hydroxide for complete neutralisation, whence the equivalent of the acid was 194.9, the calculated number for a monobasic acid, C₁₁H₁₈O₃, being 198.

In spite of the fact that pure cyanocarvomenthone was used in preparing this substance, the crude acid was certainly a mixture, and only yielded a pure compound after repeated crystallisation. Doubtless, as in the case of the hydrolysis of cyanodihydrocarvone, two stereoisomeric acids are formed, but owing to the comparatively small quantity of material at hand it was not in this instance found possible to isolate both.

The pure compound with which the analysis was made is but slightly

soluble in water or light petroleum, but dissolves somewhat readily in chloroform, benzene, ether, or alcohol, and separates from carbon tetrachloride in prisms which melt sharply at 146—147°.

The crystals, examined in polarised light, extinguish in directions which vary according to their orientation.

Fused between glass slips, it solidifies slowly on cooling to areas of parallel needles. In convergent polarised light, the interference figure associated with a crystal of wide axial angle is sometimes indistinctly to be seen. The double refraction is weak.

For the determination of the optical activity of the acid, 0.3808 gram dissolved in ethyl acetate and made up to 25 c.c. was examined in a 2-dem. tube at 22°. The mean rotation observed was -0.13° , whence $[\alpha]_D - 4.3$.

The acid behaves as a saturated ketonic acid. Dissolved in ice-cold sodium carbonate at the ordinary temperature and added to dilute potassium permanganate solution, the colour of the mixture is not appreciably affected for at least half an hour.

The author desires to express his indebtedness to the Research Fund Committee of the Chemical Society for a grant which defrayed much of the cost of the investigation.

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CLXXVI.—*The Acidic Constants of Some Ureides and Uric Acid Derivatives.*

By JOHN KERFOOT WOOD.

DURING the determination of the acidic constants of the methyl derivatives of xanthine (see following paper) results were obtained which appeared to be contrary to those which, on constitutional grounds, might have been expected. It was therefore considered advisable to conduct similar experiments with a number of other imino-compounds, chiefly ureides and derivatives of uric acid, with a view to finding the influence which other groups have on the acidity of the imino-group. The results of these experiments, together with the conclusions drawn from them, form the subject of the present paper.

In the case of some of the substances, the acidity was determined by

the ordinary conductivity method. The water used as solvent was specially distilled, and in no case did its conductivity exceed 1.5×10^{-6} at 25° .

All conductivities given in this paper are expressed in terms of reciprocal ohms.

With the majority of the substances, however, it was impossible to employ the conductivity method owing to the degree of ionisation being very small. In such cases, the dissociation constant was calculated from the velocity of saponification of methyl acetate by the sodium salt of the substance (Shields, *Zeit. physikal. Chem.*, 1893, **12**, 167). The acid was dissolved in an equivalent amount of $N/20$ sodium hydroxide and the solution then mixed with one of methyl acetate, the alkali and ester being in equivalent proportions. Portions of the mixture were removed at intervals and titrated with $N/100$ hydrochloric acid, the indicator used being *o*-nitrophenol. From the results obtained the constants were calculated by means of the equation

$$k = \frac{1}{t} \left\{ \frac{e}{e-x} - 1 - 2.302 \log \frac{e}{e-x} \right\},$$

where e represents the initial concentration of the ester and x the portion transformed in the time t . This equation can only be used satisfactorily during the middle portion of the action.

The constant k calculated as above must not be confused with the dissociation constant of the acid. It represents the product of the velocity constant (c) for the saponification of methyl acetate by sodium hydroxide and the hydrolysis constant (h) of the sodium salt of the compound under examination. Experiments on the saponification of methyl acetate by sodium hydroxide have shown that c has the value 11.42 at 25° , so that

$$h = \frac{k}{11.42}.$$

Now $h = \frac{K}{k_a}$, where K is the dissociation constant of water and k_a the dissociation constant of the acid under examination (Arrhenius, *Zeit. physikal. Chem.*, 1890, **5**, 17), and at 25° , the temperature at which all the experiments were performed, K has the value 1.2×10^{-14} . The equation finally becomes, therefore,

$$k_a = \frac{11.42 \times 1.2 \times 10^{-14}}{k}.$$

For purposes of illustration the whole of the figures obtained are given in the case of methyluracil; in the case of other substances for which this method was used only the mean values of k and k_a are given.

Methyluracil.—Trübsbach (*Zeit. physikal. Chem.*, 1895, 16, 711) determined the dissociation constant of this substance by the conductivity method and obtained a result of 4.6×10^{-9} .

The sample used by the author was prepared by Behrend's method (*Annalen*, 1885, 229, 9).

Saponification Experiment.

25 c.c. *N*/20 solution of sodium methyluracil + 25 c.c. *N*/20 solution of methyl acetate.

Time.	Titre.	<i>k</i> .
0	4.95	—
108	3.70	0.000425
179	3.40	0.000449
208	3.31	0.000447
262	3.20	0.000422
315	3.06	0.000434
Mean		0.000435

The value of k_a calculated from the above mean value of k is 3.14×10^{-10} ; this number was confirmed by subsequent experiments. The divergence from Trübsbach's result is probably explained by the difficulty of obtaining trustworthy values for the conductivity in the case of very feeble electrolytes.

α-Dimethyluracil, $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CMe} \\ \text{NH} \text{---} \text{CO} \end{smallmatrix} \text{CH}$.—This compound, which melted at 220—230°, was prepared by Behrend and Dietrich's method (*Annalen*, 1899, 309, 266). The value of k found by the saponification method was 0.00155, corresponding to a dissociation constant of 8.8×10^{-11} .

β-Dimethyluracil, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CMe} \\ \text{NMe} \text{---} \text{CO} \end{smallmatrix} \text{CH}$.—This substance was prepared by Behrend and Dietrich's method (*loc. cit.*); the sample melted at 258°.

$$k = 0.00185; k_a = 7.4 \times 10^{-11}.$$

Hydantoin.—The conductivity of this substance was determined by Trübsbach (*loc. cit.*), but the dissociation constant was not calculated. Using the figure given by him as the conductivity in *N*/128 solution, the calculated dissociation constant was found by the author to be 6.34×10^{-10} .

The hydantoin used in the present experiments was prepared by Diels and Heintzel's method (*Ber.*, 1905, 38, 305); it melted at 216—217°.

$$k = 0.000180; k_a = 7.59 \times 10^{-10}.$$

The value for k_a so determined is in good agreement with that calculated from Trübsbach's conductivity figures.

Allantoin.—This compound was prepared by the action of potassium permanganate on uric acid (Claus, *Ber.*, 1874, 7, 227).

The saponification method was used for the determination of the acidity, but a little uncertainty in the value of the constant was occasioned by the end point of the titration not being quite sharp. The mean values obtained were

$$k = 0.000117; k_a = 1.17 \times 10^{-9}.$$

Oxyuracil.—The specimen used for the experiments was prepared by Behrend's method (*Annalen*, 1885, 229, 39).

The quantity of substance available was not sufficient to allow of conductivity determinations being made, whilst the results obtained by the saponification method were not very satisfactory because of the end-point of the titration being indistinct. The mean value of k was found to be 0.0000538, corresponding to a dissociation constant (k_a) of 2.5×10^{-9} .

Parabanic Acid.—This compound was prepared by the action of nitric acid (sp. gr. 1.3) on uric acid. The product was crystallised first from ordinary distilled water and afterwards from the specially distilled water used for conductivity experiments; it was then dried at 100–105°.

Trübsbach (*loc. cit.*) made a series of experiments with this compound, and came to the conclusion that it changes in solution into urea oxalate. Owing to this change taking place, the conductivities obtained for a series of dilutions do not yield a fixed dissociation constant. The dissociation constant calculated from Trübsbach's conductivity for a $N/32$ solution is 3.74×10^{-6} . This number, however, is too high, for, using a solution of equal concentration, the author obtained a value for the conductivity which gave a dissociation constant of 0.75×10^{-6} .

The transformation of the parabanic acid into urea oxalate can be followed in the cell. The results of one experiment of this nature are shown in the following table, the concentration of the solution being $N/32$:

Time in hours.	Value of μ_{32} .	Time in hours.	Value of μ_{32} .
0	2.133	6	6.132
1	2.907	21	11.953
3	4.412	144	30.572

It will be seen that the rate of transformation of the parabanic acid is comparatively slow, so that the quantity which undergoes change during the short period of time necessary to dissolve the acid and raise the temperature of the solution to 25° must be of small dimensions. It follows, therefore, that the number given above for the dissociation constant cannot be much in excess of the true value.

Barbituric Acid.—Trübsbach (*loc. cit.*) found the dissociation constant of this substance to be 9.79×10^{-5} . Hantzsch and Vægelen (*Ber.*, 1902, 35, 1006) determined the conductivity both in aqueous and in aqueous alcoholic solutions, obtaining in the case of the former a value for μ_{64} of 27.06.

The barbituric acid used for the present experiments was prepared by Fischer and Diltthey's method (*Annalen*, 1904, 335, 334) by condensing malonic ester and urea with sodium ethoxide.

The conductivity method yielded a value for k_a of 10.51×10^{-5} , in close agreement with the number obtained by Trübsbach. The saponification method was not available in this instance, because of the action of barbituric acid on indicators.

5-Ethylbarbituric Acid.—This compound was prepared by heating to 100° for two to three hours a mixture of urea, ethylmalonic acid, and phosphoryl chloride (Conrad and Guthzeit, *Ber.*, 1882, 15, 2845). The product obtained was mixed with a small amount of water, the solution filtered off, and the residue repeatedly crystallised, first from ordinary distilled water and then from conductivity water.

A $N/64$ solution was found to have a molecular conductivity of 18.23, corresponding to a value for k_a of 3.83×10^{-5} . Owing to the fact that the solution oxidises in the cell, a series of dilution experiments was not performed.

As with the parent substance, the saponification method was not available, because of the indicators being affected by the acid.

5:5-Dimethylbarbituric Acid.—This compound was prepared by condensing dimethylmalonic ester and urea by means of sodium ethoxide (Fischer and Diltthey, *loc. cit.*). The product was crystallised from conductivity water.

For this substance also the conductivity method was found to be the more suitable. The molecular conductivity of a $N/64$ solution was found to be 0.912, giving a value for k_a of 7.3×10^{-8} .

5:5-Diethylbarbituric Acid.—The method used for the preparation of this compound was similar to that employed for the dimethyl derivative. The sample melted at 187° . After repeated crystallisation from ordinary distilled and conductivity water, the conductivity of a $N/64$ solution was determined. The molecular conductivity was found to be 0.573, giving a value for k_a of 3.7×10^{-8} .

Alloxan.—Trübsbach (*loc. cit.*) also determined the conductivity of this substance, but the dilution experiments performed by him did not give a fixed value for the dissociation constant. The value calculated from the conductivity in $N/64$ solution was 4.11×10^{-5} .

The alloxan used by the author was supplied by Kahlbaum and, after being recrystallised from conductivity water, was dried first in the desiccator and then at 120° . A $N/64$ solution had a molecular

conductivity of 2.156, giving a dissociation constant of 2.32×10^{-7} . The alloxan was found to undergo, in solution, the same kind of change as was noticed with parabanic acid. After five minutes the molecular conductivity rose from 2.156 to 2.466, whilst after fourteen hours it had a value of 11.45. Probably this fact partly accounts for the high value obtained by Trübsbach for the dissociation constant of alloxan.

Succinimide.—The sample used was prepared by the distillation of ammonium succinate.

By means of the saponification method the following values were obtained :

$$k = 0.00453 ; k_a = 3.02 \times 10^{-11}.$$

Phthalimide.—This substance was supplied by Kahlbaum.

The saponification method could not be used because of the action of the phthalimide on the indicator. A portion of the substance was recrystallised from alcohol and ether and, after drying at 120° , the conductivity of the recrystallised product was determined. The strongest solution which could be prepared had a concentration of $N/256$; the molecular conductivity of this solution was found to be 1.99, giving a dissociation constant of 1.09×10^{-7} . The conductivity of the solution was found to increase either when it was kept in the cell or in a stoppered flask. After standing sixty hours in a closed flask the molecular conductivity had increased to 3.83, whilst after about five days it had risen to 8.1.

Summary of Results.

Substance.	Dissociation constant $\times 10^7$.
Barbituric acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH}_2$	1051.0
5-Ethylbarbituric acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CHEt}$	383.0
Parabanic acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array}$	7.5
Alloxan, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CO}$	2.32
Phthalimide, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \text{NH}$	1.09
5 : 5-Dimethylbarbituric acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CMe}_2$	0.73
5 : 5-Diethylbarbituric acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CEt}_2$	0.37
Oxyuracil, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CH}_2 \\ \text{NH} - \text{CO} \end{array} \text{CO}$	0.025

Summary of Results (continued).

Substance.		Dissociation constant $\times 10^7$.
Allantoin, CO	$\begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \\ \\ \text{NH} \cdot \text{CO} \end{array}$	0·0117
Hydantoin, CO	$\begin{array}{c} \text{NH} \cdot \text{CH}_2 \\ \\ \text{NH} \cdot \text{CO} \end{array}$	0·00759
Methyluracil, CO	$\begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{NH} \cdots \text{CO} \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{CH} \end{array}$	0·00314
α -Dimethyluracil, CO	$\begin{array}{c} \text{NMe} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{NH} \cdots \text{CO} \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{CH} \end{array}$	0·00088
β -Dimethyluracil, CO	$\begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{NMe} \cdots \text{CO} \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{CH} \end{array}$	0·00074
Succinimide,	$\begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \\ \text{CH}_2 \cdot \text{CO} \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{NH} \end{array}$	0·000302

Discussion of Results.

The great diversity of the results contained in the preceding table is very striking; the first-mentioned compound is an acid six times as strong as acetic acid, whilst the last substance, succinimide, only possesses one-quarter of the acidity of phenol. A closer examination will show that the substances forming the table can be divided into four groups, as follows:

(1) Barbituric acid and 5-ethylbarbituric acid, both of which have dissociation constants greatly in excess of the others.

(2) Parabanic acid, alloxan, 5:5-dimethylbarbituric acid and 5:5-diethylbarbituric acid.

(3) Oxyuracil, allantoin, hydantoin, methyluracil, α -dimethyluracil, and β -dimethyluracil, all of which have dissociation constants much lower than those possessed by the members of group (2).

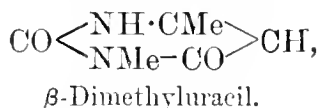
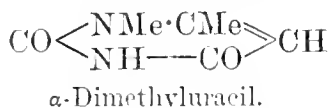
(4) The simple imides, phthalimide and succinimide.

Reserving until later a consideration of group (1), a comparison of the constitution of the members of groups (2) and (3) will show that in all cases the members of the former class contain the grouping

$\text{CO} \begin{array}{c} \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \cdot \\ \diagdown \quad \diagup \end{array}$, whereas in no member of the latter class is this grouping present. In the presence of this grouping we have a probable explanation of the greater acidity possessed by members of the second compared with that possessed by members of the third group. Each of the imino-groups contained in the above-mentioned grouping, being connected with two carbonyl groups, will be possessed of acidic properties, whereas in substances of the third class there is only one

such imino-group, the other not being attached to two carbonyl groups and having accordingly much feebler acid properties. It is well known that in the case of certain dibasic carboxylic acids, for example, succinic acid, the two carboxyl groups mutually reinforce each other and thus give rise to a dissociation constant which is of greater magnitude than would have been the case in the absence of such stereochemical influence. It appears extremely probable that in substances which contain two acidic imino-groups there will be a similar mutual reinforcement, and consequently such substances will have higher dissociation constants than substances of a similar type which only contain one such group.

The results given by the three methyluracils are in accordance with what might have been expected on constitutional grounds. The introduction of a methyl group in place of hydrogen generally causes a lowering in the acidic constant, and it will be observed that both the dimethyluracils possess smaller dissociation constants than the monomethyluracil. A comparison of the formulæ of the isomeric dimethyluracils,



shows that in the α -compound the imino-group is united to two carbonyl groups, whereas in the β -derivative it is only attached to one carbonyl group, the other nitrogen valency being satisfied by union with an unsaturated carbon atom. It would naturally be expected that the α -compound would have the greater acidity and this is confirmed by the results obtained for the two isomerides.

With regard to the two simple imides which form group four, the results obtained are also in agreement with those anticipated, phthalimide being much stronger than succinimide, just as phthalic acid is stronger than succinic acid.

Of the various results obtained none are more interesting than those given by barbituric and 5-ethylbarbituric acids. Both substances are seen to be stronger acids than acetic acid, and both can be estimated by titration with alkalis, using the ordinary indicators. The dissociation constants of these substances are, in fact, more comparable with those of the carboxylic acids than with those of the imides. Hantzsch and Voegelen (*loc. cit.*) have classed barbituric acid as a pseudo-acid. Provided that no change other than one of a tautomeric nature occurred on solution, the positive hydrogen ion of barbituric acid would be derived either from one of the imino-groups or from the methylene group. All the available evidence goes to support the latter view. In the first place, as previously mentioned, the dissociation constant is much greater than those of imino-compounds in general. The 5 : 5-dialkyl acids

contain the same two imino-groups as the original barbituric acid, and if the positive ion were derived from one of these groups, the substituted acids should be nearly as strong as the parent substance, but as is seen from the table this is by no means the case, the dissociation constant of barbituric acid being more than one thousand times as great as those of the dialkylbarbituric acids. If further proof were needed that the hydrogen ion is derived from the methylene group, it is found in the result given by 5-ethylbarbituric acid. In this substance there is still one of the hydrogen atoms of the methylene group unsubstituted, and the result is that the dissociation constant of this substance is nearly as great as that of barbituric acid. Although it may be taken as proved that the acidity of barbituric and ethylbarbituric acids is primarily due to the presence of the methylene group, no explanation of the fact can as yet be given. It does not appear to be due simply to the presence of the grouping $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$, for other substances which contain the same grouping, for example, malonic ester and acetoacetic ester, are almost devoid of acid properties.

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CLXXVII.—*The Affinity Constants of Xanthine and its Methyl Derivatives.*

By JOHN KERFOOT WOOD.

IN a previous paper (Trans., 1903, 83, 568) the author gave the results of the determinations of the affinities of a number of feeble bases, including, amongst others, several members of the xanthine series. Some of the values obtained for these xanthine derivatives were not in agreement with those expected on constitutional grounds. It was therefore decided to repeat some of the earlier experiments, and to extend the investigation so as not only to include other methyl derivatives of xanthine, but also to determine the acidic dissociation constants as well as the basic constants.

Particulars Regarding the Substances Employed.

Xanthine.—A portion of the same sample as was used in the earlier experiments (*loc. cit.*) was employed.

Heteroxanthine.—This substance was prepared by Fischer's method (*Ber.*, 1897, 30, 2,400).

Theobromine.—The sample used was obtained from Merck.

Theophylline.—This substance was also obtained from Merck. The sample was crystallised from water and then dried at 140° .

Paraxanthine.—This compound was prepared by Fischer's method (*loc. cit.*).

Caffeine.—The sample used was supplied by Kahlbaum. It melted at 234° .

Determinations of Basic Constants.

The methods used were those based on :

(1) The catalysis of methyl acetate (see Walker and Wood, *Trans.*, 1903, **83**, 484).

(2) The solubility in water and in hydrochloric acid of known concentration.

The majority of the experiments, as previously, were conducted at 40.1° , but a few determinations were also made at 25° .

Xanthine.—The basic constant of this substance, as in the earlier experiments, was determined by the solubility method. The following results were obtained at 40.1° .

1000 c.c. water dissolved 0.1823 gram xanthine.

1000 c.c. *N*/10 hydrochloric acid dissolved 0.2183 gram xanthine.

These figures give a value for the basic dissociation constant (k_b) of $1.933 \times K$, where K is the dissociation constant of water. The value of K at 40.1° is 3.15×10^{-14} (Kohlrausch and Heydweiller, *Zeit. physikal. Chem.*, 1894, **14**, 317), and therefore $k_b = 6.09 \times 10^{-14}$. This figure is of the same dimensions, but of rather greater magnitude, than that previously determined, viz., 4.6×10^{-14} .

Heteroxanthine.—Determinations of the solubility at 40.1° gave the following results :

1000 c.c. water dissolved 0.7325 gram heteroxanthine.

1000 c.c. *N*/10 hydrochloric acid dissolved 1.003 gram heteroxanthine.

Therefore $k_b/K = 3.754$ and $k_b = 11.82 \times 10^{-14}$.

Theobromine.—Repeated determinations of the solubility of theobromine in water gave a result greater than that previously obtained ; the value, however, for the solubility in hydrochloric acid was in close agreement with that already given. The following are the mean values obtained :

1000 c.c. water dissolved, at 40.1° , 0.8125 gram theobromine.

1000 c.c. *N*/10 hydrochloric acid dissolved, at 40.1° , 0.939 gram theobromine.

From these figures the following values are given :

$$k_b/K = 1.47 ; k_b = 4.63 \times 10^{-14}.$$

The greater value obtained for the solubility in water on the present

occasion has caused the value of k_b to fall to about one-quarter of the figure previously determined.

Theophylline.—With this substance it was found possible to employ both the previously mentioned methods.

Velocity Constants at 25°.

<i>N</i> /20 solution of theophylline hydrochloride + methyl acetate	0·0001276
<i>N</i> /20-Cl solution (90 per cent. HCl, 10 per cent. KCl) + methyl acetate...	0·0001225
<i>N</i> /20-Cl solution (95 ,, ,, 5 ,, ,,) + methyl acetate...	0·0001328

Calculating from these results, a *N*/20 solution of theophylline hydrochloride is hydrolysed to the extent of 92·52 per cent. at 25°.

Velocity Constants at 40·1°.

<i>N</i> /20 solution of theophylline hydrochloride + methyl acetate	0·0005333
<i>N</i> /20-Cl solution (90 per cent. HCl, 10 per cent. KCl) + methyl acetate...	0·0005140
<i>N</i> /20-Cl solution (95 ,, ,, 5 ,, ,,) + methyl acetate...	0·0005460

These results show a *N*/20 solution of theophylline hydrochloride to be hydrolysed to the extent of 92·57 per cent. at 40·1°.

Results of Solubility Determinations.

Temperature.	Grams of theophylline per 1000 c.c. of water.	Grams of theophylline per 1000 c.c. of <i>N</i> /10-hydrochloric acid.
25°	6·607	7·43
40·1	14·23	15·70

It is interesting to observe how much more soluble is theophylline than most of the other members of this series; caffeine, in fact, is the only other member possessed of a solubility comparable with that of theophylline.

The values of the ratio k_b/K , calculated from the foregoing data, are given in the following table:

	25°.	40·1°.
Methyl acetate catalysis method ...	1·74	1·734
Solubility method.....	1·305	1·125

The results, it will be observed, are all of the same dimensions. Probably most reliance can be placed on those arrived at by the methyl acetate method, in which errors are not as likely to occur as in the solubility method; a slight error in the determination of one of the solubilities would cause a proportionately greater error in the value of k_b/K . In the case of the results obtained by the catalysis method, it will be noticed that the value of k_b/K is unaffected by a change of temperature. Taking the value of k_b/K found by the catalysis method, the basic dissociation constant of theophylline at 40·1° is calculated to be $5·46 \times 10^{-14}$.

Paraxanthine.—With this substance it was impossible to prepare a solution of sufficient concentration to permit of the methyl acetate method being employed. Determinations of the solubility at 40.1° gave the following results:

1000 c.c. water dissolved 1.06 grams paraxanthine.

1000 c.c. $N/10$ hydrochloric acid dissolved 1.17 grams paraxanthine.

From these figures the following values are obtained:

$$k_b/K = 1.044; k_b = 3.29 \times 10^{-14}.$$

Caffeine.—A determination by the methyl acetate catalysis method showed caffeine hydrochloride to be hydrolysed to the extent of 89.7 per cent. in $N/10$ solution at 40.1°. This figure is identical with that previously determined (*loc. cit.*). Therefore, as previously found, $k_b = 4.0 \times 10^{-14}$.

Determination of Acidic Constants.

The method chiefly employed was that of the saponification of methyl acetate by the sodium salt of the substance (Shields, *Zeit. physikal. Chem.*, 1893, 12, 167), the results being calculated by means of the equation given in the preceding paper. The velocity of saponification of methyl acetate being much greater than that of the catalysis of the same substance, and the velocity increasing with the temperature, the determinations were made at 25°, instead of at 40.1° as in the case of the determination of the basic constants. With one or two substances the acidic constant was calculated from the solubilities in water and in $N/20$ sodium hydroxide; these solubility experiments were conducted at 40.1°.

Xanthine.—The solubility method was employed, and the following results obtained:

1000 c.c. water dissolved 0.1823 gram xanthine.

1000 c.c. $N/20$ sodium hydroxide dissolved 6.405 grams xanthine.

From these data it is found that $k_a/K = 3767$, and therefore at 40.1° $k_a = 1.186 \times 10^{-10}$.

Heteroxanthine.—With this substance also the solubility method was employed.

1000 c.c. water dissolved 0.7325 gram heteroxanthine.

1000 c.c. $N/20$ sodium hydroxide dissolved 7.781 grams heteroxanthine.

Therefore $k_a/K = 1276$ and $k_a = 4.019 \times 10^{-11}$.

Theobromine.—The determination of the velocity with which the sodium salt of this compound saponifies an equivalent quantity of

methyl acetate is rendered more difficult by the slight solubility of the compound. After the action has proceeded to some extent, the theobromine, being no longer kept in solution as the sodium salt, begins to be precipitated. The conditions of equilibrium are thus changed, and it is impossible to obtain readings at the most trustworthy part of the change, namely, the middle portion. It is possible, however, to obtain a very good estimate of the velocity of saponification by comparing the readings during the initial period of the saponification of methyl acetate by solutions, of equal concentration, of sodium theobromine and sodium phenoxide respectively.

The figures for the two reactions are shown below; in both cases 25 c.c. of the solution of the alkali salt were mixed with an equal volume of the solution of methyl acetate.

N/25 sodium theobromine + *N*/25 methyl acetate :

Time.	Titre.	<i>k</i> .
0	7.92	—
61	5.72	0.00097
81	5.39	0.00104
117	4.95	0.00111

N/25 sodium phenoxide + *N*/25 methyl acetate :

Time.	Titre.	<i>k</i> .
0	7.92	—
63	5.85	0.00080
82	5.47	0.00093
119	5.10	0.00094

It will be observed that the values obtained for *k* are in both cases of gradually increasing magnitude. Such inconstancy is always noticed when results are calculated from observations made during the initial period of the reaction. The rate of increase of *k* is almost the same in both series, the ratios between corresponding figures of the first and second series being respectively 1.21, 1.12, and 1.18. It is evident, therefore, that the saponification of the ester by the salt of theobromine is proceeding at a rate which, on the average, is 1.17 times as great as that with which the saponification by sodium phenoxide proceeds. The velocity of saponification being inversely proportional to the acidic dissociation constant, and the dissociation constant of phenol at 25° being 1.3×10^{-10} (Walker and Cormack, *Trans.*, 1900, 77, 18), it follows that the acidic dissociation constant of theobromine is approximately 1.11×10^{-10} .

Theodor Paul (*Arch. Pharm.*, 1901, 239, 48) calculated the dissociation constant at 18° from the results of determinations of the solubility in water and in solutions of sodium hydroxide. The result obtained was 1.33×10^{-8} , but an error appears to have been made in

the calculation. A recalculation by the author from Paul's data gave a value for k_a of 0.91×10^{-10} , which, allowing for the difference in temperature, is in good agreement with the value given above.

Theophylline.—No difficulty of the kind experienced with theobromine was met with in the case of theophylline, and it was therefore possible to calculate the dissociation constant from the readings obtained during the middle period of the saponification. The results obtained were as follows:

$$k = 0.0000845; k_a = 1.62 \times 10^{-9}.$$

Experiments on the solubility of theophylline in water and sodium hydroxide were made. It was found that the additional amount of theophylline which passed into solution because of the presence of the alkali was equivalent to the amount of the latter, thus showing that theophylline is a comparatively strong acid, the sodium salt of which is not appreciably hydrolysed in solution.

Paraxanthine.—For this substance also, the saponification method was employed, giving as results:

$$k = 0.0000616 \text{ and } k_a = 2.22 \times 10^{-9}.$$

Caffeine.—This compound is almost devoid of acidic properties. A solution of it in sodium hydroxide saponified methyl acetate with a velocity almost as great as that shown by the pure alkali. Moreover, the solubility in a solution of sodium hydroxide is only very slightly greater than that in pure water. The value of k_a is evidently, therefore, of dimensions less than 1×10^{-14} .

Summary of Results.

		$k_b \times 10^{14}$	Temp.	$k_a \times 10^{11}$	Temp.
Xanthine,	$\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ \quad \parallel \\ \text{CO} \cdot \text{NH} \cdot \text{C} - \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH} \dots\dots$	4.6	40.1°	11.86	40.1°
Heteroxanthine,	$\begin{array}{c} \text{NH} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \quad \parallel \\ \text{CO} \cdot \text{NH} \cdot \text{C} - \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH} \dots$	11.82	40.1	4.019	40.1
Theobromine,	$\begin{array}{c} \text{NH} - \text{CO} - \text{C} \cdot \text{NMe} \\ \quad \parallel \\ \text{CO} \cdot \text{NMe} \cdot \text{C} - \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH} \dots$	4.63	40.1	11.1	25.0
Theophylline,	$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ \quad \parallel \\ \text{CO} \cdot \text{NMe} \cdot \text{C} - \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH} \dots\dots$	5.46	40.1	162.0	25.0
Paraxanthine,	$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \quad \parallel \\ \text{CO} - \text{NH} - \text{C} - \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH} \dots$	3.29	40.1	222.0	25.0
Caffeine,	$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NMe} \\ \quad \parallel \\ \text{CO} \cdot \text{NMe} \cdot \text{C} - \text{N} \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{CH} \dots\dots$	4.0	40.1	<0.001	25.0

Before comparing in any way the results given in the above table, one or two points require to be specially mentioned. The methods used for the determination both of the basic and the acidic constants have not been the same for all the substances examined, and it might perhaps be urged that this difference in method made any comparison of the results of uncertain value. This objection vanishes, however, when it is recalled that for each series of constants the results for one substance have been arrived at by both methods. Thus, in the case of the basic constants, the constant of theophylline was determined both by the methyl acetate catalysis method and by the solubility method, the values obtained being of similar dimensions. In the case of the acidic constants, the fact that the dissociation constant of theobromine as found by the saponification method is in close agreement with that of the same substance calculated from Paul's solubility data shows that the results arrived at by the two methods are strictly comparable.

The effect of temperature on the results must also be referred to, seeing that in the case of the acidic constants results are given at two temperatures. This difference in the working temperature was largely due to the desire to obtain results of the greatest possible accuracy. A comparatively low temperature was found to be the best in the case of the saponification method, whilst in the case of the solubility method it was considered that, the solubilities of some of the substances being very small, more accurate results could be obtained by working at a higher temperature. For purposes of comparison, it will be sufficient to state that at 40.1° k_a will have a value rather greater than twice the value which it has at 25° ; this result was arrived at by experiments made with theophylline by the saponification method.

Discussion of Results.

It has been pointed out by Walker (Trans., 1903, 83, 182; *Proc. Roy. Soc.*, 78, A, 140) that the value k_b is a composite expression containing not only the real ionisation constant of the base, but also a hydration constant. If the hydration remained constant, it might be expected that the values of k_b would gradually increase as the number of methyl groups in the xanthine nucleus increased. It seems reasonable to suppose that with substances of similar constitution such as those examined the degree of hydration will not vary to any great extent, and on this assumption it will be evident that there can likewise be no great difference in the values of the true ionisation constants, since for all the substances k_b has nearly the same magnitude.

The matter becomes simpler when acids are under consideration, for in such cases the process of hydration does not as a rule form part of the operation of solution. The general effect of the substitution of a hydrogen atom by a methyl group might be expected to be a very slight diminution in the value of the acidic constant, and it will be observed that in the transition from xanthine to heteroxanthine such an effect on the value of k_a is produced. But when we proceed further and replace a second hydrogen atom by a methyl group, it is observed that k_a , instead of undergoing a further slight diminution, assumes in all cases a much greater value, the increase being most noticeable in the cases of paraxanthine and theophylline. The imino-groups which are now strongly acidic were present in the parent substance xanthine, and yet that substance has an acidic dissociation constant which is only a small fraction of those possessed by the dimethylxanthines. This great augmentation of the value of k_a can only be explained by the assumption of some stereochemical change taking place on the introduction of the second methyl group, the change produced being least when substitution takes place at position 3 of the xanthine nucleus.

The almost complete freedom from acid characteristics shown by caffeine is in accordance with what might be expected on constitutional grounds, since it contains no imino-group.

A comparison of the values of k_a given by the isomeric dimethylxanthines is also of interest when taken in conjunction with their respective constitutions. From our general knowledge as to the negative character of the carbonyl group, it might have been reasonably expected that theobromine, in which the imino-group is attached to two carbonyl groups, would possess a value for k_a greater than those given by paraxanthine and theophylline, in both of which substances the imino-group is only connected with one carbonyl group. This view is supported by some of the results described in the previous paper; for example, those obtained with the dimethyluracils. The results obtained, however, with the dimethylxanthines show that the positions are entirely reversed, paraxanthine having the highest and theobromine the lowest value for k_a . Were it not for the fact that the constitution of these substances appear to have been fixed with certainty by Fischer and others, it might almost be believed that some confusion between the two had taken place, and that theobromine should really have the formula ascribed to paraxanthine, and *vice versa*. In the circumstances, however, this view cannot be entertained, and we must therefore conclude that in the case of the dimethylxanthines the ordinary influences of the carbonyl group are not seen because of the stereochemical influence of the methyl groups being more powerful and

varying in magnitude according to the positions in the xanthine nucleus occupied by the methyl groups.

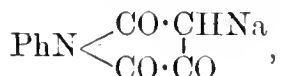
In view of the interesting results obtained, the investigation is being extended to other purine derivatives.

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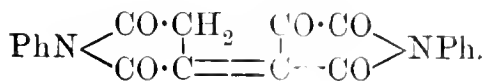
CLXXVIII.—*Xanthoxalanil and its Analogues.*

By SIEGFRIED RUEHMANN.

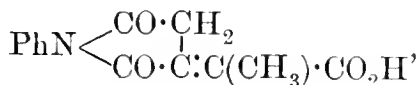
RECENTLY (Trans., 1906, 89, 1236) it has been shown that the yellow product which W. Wislicenus and Sattler (*Ber.*, 1889, 24, 1245) obtained by the action of sodium ethoxide on a mixture of ethyl oxalate and acetanilide had the composition $C_{20}H_{12}O_5N_2$; it was found also that similar compounds could be prepared by using, instead of acetanilide, the acetyl derivatives of *o*-toluidine, *p*-toluidine, and α -naphthylamine. This reaction has now been applied to the production of analogous substances from the acetyl derivatives of *m*-xylidine, pseudocumidine, β -naphthylamine, and *p*-aminophenetole. It was suggested (*loc. cit.*) that the formation of xanthoxalanil was preceded by the production of sodio-oxalacetanil,



which, on treatment with a mineral acid, yielded the coloured condensation product. Its constitution accordingly was represented by the formula



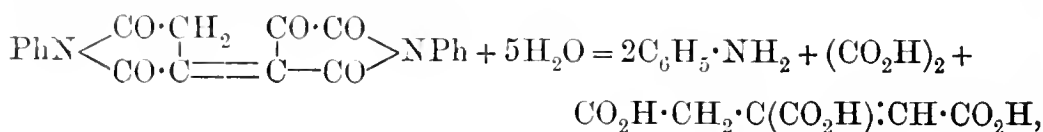
This view concerning the mode of formation of xanthoxalanil induced me to examine whether the solution of sodio-oxalacetanil, when treated with pyruvic acid, instead of with a mineral acid, furnished the compound



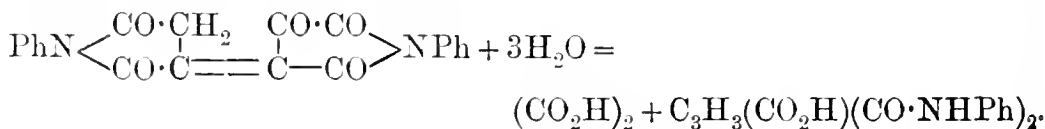
just as indoxyl condenses with the ketonic acid to yield the corresponding indogenide; I found, however, that this reaction did not take place, but that in this case also xanthoxalanil was formed.

In my previous communication (*loc. cit.*, p. 1239) I pointed out that

xanthoxalanil, on heating with an alkali, might be expected to undergo the following decomposition :



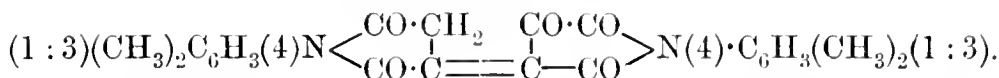
and furnish aconitic acid or its stereoisomeride. W. Wislicenus and Sattler (*loc. cit.*) had already studied this reaction ; they stated that the compound was completely decomposed by caustic potash and yielded, besides aniline and oxalic acid, a mixture of volatile organic acids which reduced silver solutions, but they did not succeed in proving the presence of acetic acid which they expected to be formed. On repeating this experiment I was able to prove that the alkaline solution, which was produced by the action of caustic potash on xanthoxalanil, contained oxalic acid and dianilaconitic acid. Their formation might be represented by the equation



Similar to the decomposition of xanthoxalanil is the behaviour of alkalis towards its analogues ; thus from xanthoxalo-*m*-xylidil, *m*-dixylil-acconitic acid could be obtained. On hydrolysis of dianilaconitic acid with concentrated hydrochloric acid, aconitic acid is produced. These facts support the constitution of xanthoxalanil and its analogues which I put forward from the mode of their formation.

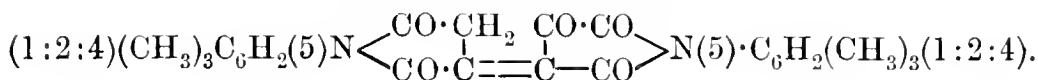
These compounds when reduced with zinc dust and acetic acid, are transformed into colourless substances. Up to the present I have isolated the reduction product which is formed from *m*-xanthoxalo-*m*-xylidil. Its composition, $\text{C}_{24}\text{H}_{26}\text{O}_5\text{N}_2$, indicates that, under the influence of the reducing agent, the yellow condensation product has united with six atoms of hydrogen. There cannot be any doubt that two of them are united with the unsaturated group of the molecule of the yellow compound ; I hope to be able to ascertain the position of the other four hydrogen atoms in the reduced substance by examining the behaviour of this substance towards alkalis. The results of this examination, and of the further study of xanthoxalanil and its analogues, will be published shortly.

EXPERIMENTAL.

Xanthoxalo-m-xylylidil,


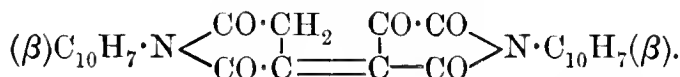
This substance is prepared in the same way as xanthoxalanil by adding ethyl oxalate to sodium ethoxide suspended in dry benzene, and mixing the solution which is thus produced with aceto-*m*-xylylide dissolved in benzene. The product, after standing for several days, is shaken with water, the aqueous layer filtered and treated with an excess of dilute hydrochloric acid, when a yellow solid is precipitated in the course of a few hours. This is readily soluble in hot nitrobenzene, sparingly, however, in boiling glacial acetic acid, and, on cooling, crystallises from either solution in yellow plates which melt and decompose at about 244° after having begun to darken a few degrees before :

0.2280 gave 13.6 c.c. moist nitrogen at 20° and 756 mm. $\text{N} = 6.78$.
 $\text{C}_{24}\text{H}_{20}\text{O}_5\text{N}_2$ requires $\text{N} = 6.73$ per cent.

Xanthoxalo-ψ-cumidil,


Aceto-ψ-cumidide reacts with sodium ethoxide and ethyl oxalate under the same conditions as the former compound, and yields a yellow condensation product. This is very readily soluble in hot nitrobenzene, but sparingly so in boiling glacial acetic acid, and, on cooling, crystallises in yellow prisms which begin to darken at 220° and melt at about 250° with decomposition :

0.2014 gave 0.5190 CO_2 and 0.0990 H_2O . $\text{C} = 70.28$; $\text{H} = 5.46$.
 0.2498 „ 14 c.c. moist nitrogen at 18° and 757 mm. $\text{N} = 6.44$.
 $\text{C}_{26}\text{H}_{24}\text{O}_5\text{N}_2$ requires $\text{C} = 70.27$; $\text{H} = 5.40$; $\text{N} = 6.30$ per cent.

Xanthoxalo-β-naphthylanil,


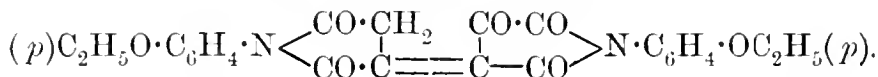
This substance is formed from aceto-β-naphthalide in the same way as its stereoisomeride. It differs from it inasmuch as it dissolves in boiling nitrobenzene with great difficulty, and, on cooling, crystallises in bronze-coloured, shining plates which decompose at about 290° :

0.2013 gave 0.5375 CO₂ and 0.0635 H₂O. C = 72.82 ; H = 3.53.

0.2192 „ 12.2 c.c. moist nitrogen at 27° and 760 mm. N = 6.14.

C₂₈H₁₆O₅N₂ requires C = 73.0 ; H = 3.47 ; N = 6.08 per cent.

Xanthoxalo-p-ethoxylanil,



This compound is prepared in the same way as the former substances by the action of phenacetin on ethyl oxalate in the presence of sodium ethoxide. Owing to the fact that phenacetin is sparingly soluble in benzene, a large quantity of the solvent is required. The condensation product is sparingly soluble in glacial acetic acid, but readily so in hot nitrobenzene, and, on cooling, crystallises in orange plates which melt at about 260° with decomposition :

0.2493 gave 13.6 c.c. moist nitrogen at 18° and 755 mm. N = 6.25.

C₂₄H₂₀O₇N₂ requires N = 6.25 per cent.

Action of Alkalis on Xanthoxalanil and its Homologues.

On digesting xanthoxalanil with dilute caustic potash on the water-bath, it dissolves and deposits an oil which was identified as aniline. The yellow alkaline solution, after removal of the aniline by extraction with ether, when treated with an excess of dilute hydrochloric acid, yields a solid. This dissolves in sodium carbonate and is precipitated on adding an acid to the solution. This property has been made use of for purifying the compound. It is readily soluble in alcohol, and crystallises from this solution in bunches of colourless needles which melt at 199—200° after having begun to soften a few degrees before :

0.2048 gave 0.4992 CO₂ and 0.0913 H₂O. C = 66.48 ; H = 4.95.

0.2116 „ 16.4 c.c. moist nitrogen at 25° and 769 mm. N = 8.75.

C₁₈H₁₆O₄N₂ requires C = 66.67 ; H = 4.94 ; N = 8.64 per cent.

The behaviour of this substance, which is recorded below, characterises it as dianilaconitic acid. Michael (*Amer. Chem. J.*, 1887, 9, 192) obtained a compound with this formula by allowing an aqueous solution of the dianiline salt of aconitic acid to remain for some time at the ordinary temperature ; he stated that it crystallised from alcohol in long, prismatic needles, which had a faint pink shade and melted at 188—189°. These properties of Michael's dianilaconitic acid hardly differ from the behaviour of the substance which I obtained from xanthoxalanil except in the melting point. Indeed, isomeric dianil derivatives would correspond to a compound having the

same structure as aconitic acid, but a closer comparison of the two substances will be necessary before they can be regarded as different.

The production of dianilaconitic acid from xanthoxalanil is accompanied by the formation of oxalic acid. This is contained in the acid filtrate from the derivative of aconitic acid; it was characterised by a calcium determination of the salt which is precipitated from the solution by means of ammonia, calcium chloride, and acetic acid:

0.4410, on ignition, left 0.1695 CaO. $\text{CaO} = 38.43$.

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ requires $\text{CaO} = 38.35$ per cent.

That the compound which is formed from xanthoxalanil is indeed dianilaconitic acid follows from its behaviour on hydrolysis, when aconitic acid and aniline are produced. This decomposition may be effected by caustic potash, as is indicated already by the fact that aniline is formed on digesting xanthoxalanil with the alkali, but it is preferable to use concentrated hydrochloric acid for this purpose. The solid dissolves after two to three hours' boiling with the acid. The solution, when cold, is extracted several times with ether and the ethereal solution decolorised with animal charcoal; on evaporating the ether, colourless crystals of an acid separate which was identified as aconitic acid by the melting point ($186-187^\circ$) and by the analysis of the silver salt:

0.2520, on ignition, left 0.1642 Ag. $\text{Ag} = 65.15$.

$\text{C}_6\text{H}_3\text{O}_6\text{Ag}_3$ requires $\text{Ag} = 65.45$ per cent.

Di-m-xylydilaconitic Acid, $\text{C}_3\text{H}_3(\text{CO}_2\text{H})[\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2]_2$.

On digesting xanthoxalo-*m*-xylydil with dilute aqueous caustic potash, it turns red and then rapidly dissolves. The yellow solution, when treated with an excess of dilute hydrochloric acid, yields a solid which readily dissolves in boiling alcohol and, on cooling, crystallises in bunches of colourless needles; these, after recrystallisation from the same solvent, melt at $196-197^\circ$ with evolution of gas:

0.2193 gave 14.4 c.c. moist nitrogen at 20° and 758 mm. $\text{N} = 7.49$.

$\text{C}_{22}\text{H}_{24}\text{O}_4\text{N}_2$ requires $\text{N} = 7.37$ per cent

Reduction of Xanthoxalo-m-xylydil.

The boiling solution of xanthoxalo-*m*-xylydil in glacial acetic acid is decolorised by zinc dust; on adding water to the filtrate, a solid is precipitated which dissolves slowly in cold sodium carbonate solution with the exception of a small quantity of a resinous product. The filtrate, when treated with an excess of hydrochloric acid, yields a

white precipitate which crystallises from dilute alcohol in colourless plates melting at $160-161^{\circ}$:

0.2013 gave 0.5025 CO_2 and 0.1118 H_2O . C = 68.13; H = 6.17.

0.2020 „ 0.5055 CO_2 „ 0.1121 H_2O . C = 68.24; H = 6.16.

0.2116 „ 12.2 c.c. moist nitrogen at 17° and 755 mm. N = 6.64.

$\text{C}_{24}\text{H}_{26}\text{O}_5\text{N}_2$ requires C = 68.24; H = 6.16; N = 6.63 per cent.

The substance is fairly soluble in cold alcohol, readily so when hot; the alcoholic solution gives with ferric chloride a deep violet coloration which, on warming, changes to red.

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CLXXIX.—*The Influence of Various Substituents on the Optical Activity of Tartramide. Part II.*

By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS, M.Sc.

IN a previous communication on the same subject, the optical activity of seventeen derivatives of tartramide has been described by one of us (P. F. Frankland and Slator, *Trans.*, 1903, **83**, 1349), but amongst these only the methylamide and ethylamide were derivatives of tartaric acid with aliphatic amines. In the present communication we have confined our attention to the latter, having prepared and examined the normal and isopropylamides, the allylamide, the normal and isobutylamides, and the normal heptylamide. The rotation of these compounds has, as before, been determined in pyridine, and, when possible, also in methyl alcohol, and in water solution.

The amides described in the present paper were prepared by the interaction in the cold of the amine with an alcoholic solution of methyl tartrate, and all were obtained as crystalline bodies of high melting point ($183-216^{\circ}$). Excepting in the case of the isopropylamide, of which only 23 per cent. of the theoretical quantity was obtained, the yields were excellent, and in the case of the isopropylamide also a better yield would no doubt have resulted if the alcohol had been evaporated off after completion of the reaction.

The results of our investigation are summarised in the following table:

Summary of Results :

	Melting point.	Pyridine.		Methyl alcohol.		Water.	
		<i>p.</i>	$[M]_D^{20}$.	<i>p.</i>	$[M]_D^{20}$.	<i>p.</i>	$[M]_D^{20}$.
Tartaric di-							
Amide.....	195°	—	—	0·0807	+ 208°	0·077	+ 160°
		—	—	0·1797	213	1·305	158
Methylamide	189	0·684	+ 274°	4·998	266	0·994	255
		7·679	279	4·986	262	10·350	242
Ethylamide	210—211	1·049	277	4·997	282	1·390	262
		5·030	279	5·001	281	7·468	256
<i>n</i> -Propylamide	216	2·196	289	2·019	290	1·808	264
		4·741	287	4·857	290	2·717	260
<i>iso</i> Propylamide	189	1·654	272	1·910	273	1·398	247
		4·665	272	4·867	272	4·682	247
Allylamide	183	2·528	251	2·900	273	2·392	247
		4·735	252	5·914	270	4·697	246
<i>n</i> -Butylamide.....	193	1·899	286	0·907	298	0·258	280
		4·801	288	4·416	291	—	—
<i>iso</i> Butylamide	183·5	1·753	295	1·007	306	0·549	275
		5·064	294	5·432	305	—	—
<i>n</i> -Heptylamide	183	1·621	304	0·9951	303	—	—
		3·579	305	—	—	—	—

With the above may be compared the previously-determined rotations of the following substitution derivatives of tartramide :

Tartaric di-	$[M]_D^{20}$.		
	Pyridine.	Methyl alcohol.	Water.
Piperidide *	± 0°	—	—
Phenylhydrazide	< + 80	—	—
Diacetyl[tartaric]- <i>o</i> -toluidide	+ 80	—	—
Hydrazide	—	—	+ 170°
<i>ac</i> -Tetrahydro- β -naphthylamide *	+ 240	—	—
Tartranil.....	+ 272	+ 268°	+ 216
Benzylamide	+ 300	—	—
Furfurylamide	+ 307	—	—
Tartaric- <i>p</i> -tolnil	+ 366	+ 280	—
Acetophenone-hydrazone	+ 397	—	—
α -Naphthylamide	+ 400	—	—
Benzylidene-hydrazide	+ 554	—	—
<i>o</i> -Toluidide	+ 667	—	—
<i>m</i> -Toluidide	+ 730	—	—
Furfurylidene-hydrazide	+ 736	—	—
Anilide	+ 739	—	—
<i>p</i> -Toluidide.....	+ 793	—	—
<i>ar</i> -Tetrahydro- β -naphthylamide *	+ 840	—	—
β -Naphthylamide	+ 1160	—	—
Methyltartramide †	—	—	+ 281·6
Ethyltartramide †	—	—	+ 264·3

* Frankland and Ormerod, Trans., 1903, **83**, 1312.
† Ladenburg, Ber., 1896, **29**, 2710.

The foregoing figures show that all the substituted tartramides, excepting the phenylhydrazide and piperidide, have a higher dextro-

rotation than tartramide itself, and that substitution by aromatic radicles leads to a dextrorotation of a much higher order than that resulting from substitution by aliphatic groups. The piperidide is inactive, at any rate in pyridine and in aniline solutions, which were the only ones in which it was examined. The benzylamide and furfurylamide have about the same rotation in pyridine as the *n*-heptylamide, whilst the *ac*-tetrahydro- β -naphthylamide has even a lower dextrorotation in pyridine than any of the alkyl-substituted tartramides.

Taking the derivatives with the aliphatic amines of the normal series, it appears that the value of $[M]_D$ does not show any evidence of having reached a maximum within the range of the series of compounds prepared, for the *n*-heptylamide has a higher molecular rotation than any of the lower homologues. The isopropylamide has a lower rotation than the *n*-propylamide, whilst the rotation of the isobutylamide is greater (excepting in water solution) than that of the *n*-butylamide.

The rotation of the allylamide as compared with that of the *n*-propylamide is particularly interesting, for it is now generally believed that the presence of a double bond in a carbon-chain leads to an increase in the optical activity (see P. Frankland and Slatore, *Trans.*, 1903, 83, 1351, where numerous references to this relationship are given). In the present case, however, the substitution of *n*-propyl by allyl is attended by a marked diminution in the rotation, and the same exceptional relationship will be shown by one of us (P. Frankland and Done) to be exhibited in the case of the *n*-propylamide and allylamide of malic acid.

The piperidide is the only secondary amide hitherto examined, and, as indicated in the above table, it was found to be practically inactive; this result naturally suggests that racemisation of the tartaric acid had taken place in the process of preparation, but it may also be due to the dextrorotation being depressed to about zero by the introduction of the piperidine group, and that this is perhaps the case is rendered less remotely possible since it has been found by one of us that in the malic series the piperidide has a much lower rotation than the unsubstituted malamide in pyridine and methyl alcohol solutions, whilst in glacial acetic acid solution the sign of the rotation is actually reversed.

EXPERIMENTAL.

Tartaric Di-n-propylamide.

An excess of *n*-propylamine was added to a concentrated solution of methyl tartrate in absolute ethyl alcohol in the cold. The separation of amide commenced in the course of a few minutes; the crystals

formed, after standing for two days, were filtered off, and a further crop was obtained by evaporating part of the alcohol. The yield was about 80 per cent. The product was purified by recrystallising from a mixture of equal parts of ethyl alcohol and ethyl acetate.

0.0946 gave 10.0 c.c. moist nitrogen at 16.5° and 761 mm. $N = 12.30$.

$C_{10}H_{20}O_4N_2$ requires $N = 12.07$ per cent.

Tartaric di-n-propylamide crystallises in colourless, flat, elongated plates, or flat needles, melting at 216° with slight decomposition. It is easily soluble in pyridine, or hot alcohol, less so in ethyl acetate, whilst in cold water the strongest obtainable solution was about 2.4 per cent.

Rotation of Tartaric Di-n-propylamide.

n_D	$d_{20^\circ/4^\circ}$	l	$\alpha_D^{20^\circ}$	$[\alpha]_D^{20^\circ}$	$[M]_D^{20^\circ}$
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Pyridine Solution.

4.741	0.9867	0.999	+ 5.79°	+ 123.9°	+ 287.4°
2.196	0.9817	1.998	5.37	124.7	289.2

Methyl Alcohol Solution.

1.857	0.8083	1.998	+ 9.79°	+ 124.8°	+ 289.5°
2.019	0.7991	1.998	4.03	124.9	289.7

Water Solution.

2.717	1.0029	0.999	+ 3.05°	+ 112.1°	+ 260.0°
1.808	1.0014	1.998	4.11	113.6	263.6

Tartaric Diisopropylamide.

The theoretical quantity of isopropylamine was added to a solution of methyl tartrate in absolute ethyl alcohol. After standing two days the liquid became viscid and yellow; the amide separated from this on cooling with ice or adding a crystal as nucleus. After standing two more days the crystals were filtered off, but only a 23 per cent. yield was obtained. The product was recrystallised from ethyl acetate to which a little alcohol had been added.

0.1130 gave 12.1 c.c. moist nitrogen at 17° and 737 mm. $N = 12.03$.

$C_{10}H_{20}O_4N_2$ requires $N = 12.07$ per cent.

Tartaric di-isopropylamide crystallises in slightly flattened needles, melting at 189° without decomposition. Its solubility in the ordinary solvents is rather greater than that of the normal propylamide.

Rotation of Tartaric Diisopropylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
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Pyridine Solution.

1.654	0.9806	1.998	+3.80°	+117.3°	+272.0°
4.665	0.9858	0.999	5.38	117.1	271.7

Methyl Alcohol Solution.

1.910	0.7970	1.998	+3.59°	+117.8°	+273.3°
4.867	0.8058	0.999	4.60	117.4	272.4

Water Solution.

1.398	1.0003	1.998	+2.98°	+106.7°	+247.4°
1.682	1.0059	0.999	5.00	106.3	246.6

Tartaric Diallylamide.

This was similarly prepared by mixture of theoretical proportions of allylamine and methyl tartrate in alcoholic solution. The amide already began to separate after an hour, and by filtering off the crystals after twenty-four hours' contact, a yield of 62 per cent. was obtained. The product was purified by recrystallisation from a mixture of equal parts of ethyl alcohol and ethyl acetate.

0.0997 gave 10.84 c.c. moist nitrogen at 15° and 745 mm. $N = 12.48$.

$C_{10}H_{16}O_4N_2$ requires $N = 12.28$ per cent.

Tartaric diallylamide crystallises in flat, thin, colourless plates melting at 183° to a pale yellow liquid. Its solubility in the common solvents is about the same as that of the *n*-propylamide.

Rotation of Tartaric Diallylamide.

<i>n.</i>	<i>d</i> 20°/4°.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
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Pyridine Solution.

2.528	0.9838	1.998	+5.48°	+110.3°	+251.4°
4.735	0.9896	0.999	5.18	110.7	252.3

Methyl Alcohol Solution.

2.960	0.8023	1.998	+5.57°	+119.8°	+273.2°
5.914	0.8092	0.999	5.66	118.4	269.9

Water Solution.

2.392	1.0036	1.998	+5.19°	+108.2°	+246.7°
4.697	1.0086	0.999	5.10	107.8	245.7

Tartaric Di-n-butylamide.

Butylamine was added in theoretical quantity to a cooled solution of methyl tartrate in ethyl alcohol. The separated amide was filtered off after the mixture had stood for about thirteen hours, a 75 per cent. yield being obtained. The product was purified by recrystallisation from a mixture of two parts of ethyl acetate to one of ethyl alcohol.

0.1482 gave 14.0 c.c. moist nitrogen at 17° and 737 mm. $N = 10.84$.

$C_{12}H_{24}O_4N_2$ requires $N = 10.77$ per cent.

Tartaric di-n-butylamide crystallises in beautiful, long, flat, needles melting at 193° without decomposition. Like the other amides described above, it is very soluble in pyridine or alcohol; its solubility in water is, however, very small (only 0.3 per cent.).

Rotation of Tartaric Di-n-butylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
<i>Pyridine Solution.</i>					
1.899	0.9809	1.998	+4.10°	+110.2°	+286.4°
4.801	0.9849	0.999	5.23	110.7	287.8
<i>Methyl Alcohol Solution.</i>					
0.907	0.7949	3.899	+3.22°	+114.6°	+297.8°
4.416	0.8033	0.999	3.97	112.0	291.3
<i>Water Solution.</i>					
0.258	0.9989	3.899	+1.08°	+107.5°	+279.5°

Tartaric Diisobutylamide.

*iso*Butylamine was added in theoretical quantity to a cooled solution of methyl tartrate in ethyl alcohol. After standing twelve hours, the amide which had separated was filtered off, the yield being about 70 per cent., whilst more was obtainable by evaporating the mother liquor.

0.1227 gave 11.8 c.c. moist nitrogen at 19° and 756.5 mm. $N = 11.01$.

$C_{12}H_{24}O_4N_2$ requires $N = 10.77$ per cent.

Tartaric diisobutylamide crystallises in small rhombic plates melting at 183.5°. It is more soluble in the ordinary organic solvents than the normal butyl- and propyl-amides, resembling the *isopropylamide* in this respect, but it is only very slightly so in water (0.8 per cent.).

Rotation of Tartaric Diisobutylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
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Pyridine Solution.

1.753	0.9805	1.998	+3.90°	+113.6°	+295.3°
5.064	0.9853	0.999	5.64	113.2	294.3

Methyl Alcohol Solution.

1.007	0.7949	3.899	+3.67°	+117.6°	+305.7°
5.432	0.8065	0.999	5.13	117.2	304.8

Water Solution.

0.549	0.9991	3.899	+2.26°	+105.6°	+274.6°
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Tartaric Di-n-heptylamide.

A theoretical quantity of *n*-heptylamine (Kahlbaum) was added to a cold solution of methyl tartrate in absolute alcohol. The mixture became a solid mass in the course of a few hours, and a theoretical yield of the amide was obtained. It was recrystallised from methylated spirit until of constant rotation. It forms elongated, flat plates melting at 183° without decomposition, and is much less soluble in most solvents than are the lower amides above mentioned. It is insoluble in water, slightly soluble in cold alcohol, and at the ordinary temperature gives only about a 4 per cent. solution in pyridine.

0.2680 gave 19.4 c.c. moist nitrogen at 12° and 728 mm. ; $N = 8.22$.

$C_{18}H_{36}O_4N_2$ requires $N = 8.14$ per cent.

Rotation of Tartaric Di-n-heptylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
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Pyridine Solution.

1.621	0.9789	2.993	+4.19°	+88.24°	+303.5°
3.579	0.9805	0.999	3.11	88.72	305.2

Methyl Alcohol Solution.

0.9951	0.7955	3.899	+2.72°	+88.14°	+303.2°
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*Rotation of Tartaric Diphenylhydrazide.**Glacial Acetic Acid Solution.*

0.5672	1.052	3.899	+1.88°	+80.85°	+266.80°
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Rotation of Tartaric Dimethylamide.

<i>p.</i>	$d\ 20^{\circ}/4^{\circ}.$	<i>l.</i>	$\alpha_D^{20^{\circ}}.$	$[\alpha]_D^{20^{\circ}}.$	$[M]_D^{20^{\circ}}.$
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Methyl Alcohol Solution.

4.998	0.8147	3.899	+23.97°	+151.0°	+265.8°
4.986	0.8147	1.998	12.08	148.8	261.9

*Rotation of Tartaric Diethylamide.**Methyl Alcohol Solution.*

4.997	0.8117	1.998	+11.20'	+138.1°	+281.7°
5.001	0.8127	1.998	11.21	137.9	281.3

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CLXXX.—*The Influence of various Substituents on the Optical Activity of Malamide.*

By PERCY FARADAY FRANKLAND and EDWARD DONE, M.Sc.

THE results recorded in this paper form part of a systematic investigation which is being made by one of us on the rotation of the amides of optically active acids, in connexion with which papers have already appeared on some substitution derivatives of glyceramide (P. Frankland, Wharton, and H. Aston, *Trans.*, 1901, **79**, 266), and of tartramide (P. Frankland and Slaton, *Trans.*, 1903, **83**, 1349; Ormerod, *Trans.*, 1903, **83**, 1342; and Twiss, preceding paper).

The present communication deals with the methyllamide, ethyllamide, normal- and *iso*-propyllamide, allyllamide, normal- and *iso*-butyllamide, and normal heptyllamide of ordinary *l*-malic acid, as well as with the piperidide, and phenylhydrazide of the same acid.

Of these derivatives, only the *n*-propyllamide has been previously prepared (McCrae, *Trans.*, 1903, **83**, 1324), whilst the anilide and the three toluidides have been described by Guye and Babel (*Arch. Sci. phys. nat.*, 1899 [iv], **7**, 23), and by Walden (*Zeit. physikal. Chem.*, 1895, **17**, 264).

The alkylamides were all prepared by the interaction of the amine with diethylmalate, either alone or in alcoholic solution, and either in the cold or at a temperature not exceeding 100°. The yields were in most cases, and especially in the case of the higher amines in which no alcohol was used, very satisfactory. As in the corresponding

derivatives of tartramide, the poorest yield was obtained in the case of the isopropylamide.

The piperidide was prepared by the prolonged heating of diethylmalate with piperidine at 130° , whilst the phenylhydrazide was prepared, on the one hand by Bülow's method, in which malic acid and phenylhydrazine are heated together at 120 — 140° , and, on the other, by Fischer and Passmore's method, in which an aqueous solution of malic acid is heated on the water-bath with a solution of phenylhydrazine in acetic acid. The products obtained by each of these methods had substantially the same rotation, showing that no racemisation occurs at the higher temperature to which the mixture is heated in the case of Bülow's method.

The rotation was in all cases, excepting that of the phenylhydrazide, determined in pyridine, in methyl alcohol, and in glacial acetic acid solution. The rotation of the phenylhydrazide was determined in pyridine and in glacial acetic acid only, in consequence of its insolubility in methyl alcohol.

The results of the polarimetric determinations are summarised in the following table:—

	Melting point.	Pyridine.		Methyl alcohol.		Glacial acetic acid.	
		<i>p.</i>	$[M]_D^{20^{\circ}}$	<i>p.</i>	$[M]_D^{20^{\circ}}$	<i>p.</i>	$[M]_D^{20^{\circ}}$
Maldi-amide *	157°	$c=1.998$	-76.2°	—	—	$c=4.678$	-59.7°
„ methylamide ...	99	4.634	89.6	6.250	-109.6°	4.267	120.9
		10.080	90.0	9.982	107.9	8.185	117.2
„ ethylamide	122	4.319	90.6	4.984	110.3	4.170	116.0
		10.250	89.1	9.177	111.8	7.995	117.2
„ <i>n</i> -propylamide .	126	4.530	90.5	5.020	114.3	4.278	115.4
		7.896	88.8	11.340	114.7	5.040	114.8
		—	—	—	—	9.048	112.8
„ isopropylamide .	150—151	2.548	69.1	3.803	92.0	3.710	92.1
		3.986	69.0	6.039	90.3	6.284	92.5
„ allylamide	117.5	4.639	72.7	4.804	102.5	4.492	86.9
		10.390	74.0	9.095	103.3	10.780	87.4
„ <i>n</i> -butylamide ...	125	3.776	87.1	5.633	116.5	5.455	106.4
		10.850	86.3	10.540	112.0	9.718	104.9
„ isobutylamide ..	121	5.394	86.9	5.316	117.4	5.492	106.2
		7.984	89.4	9.128	118.4	7.563	105.3
„ <i>n</i> -heptylamide..	131	5.166	88.6	6.001	116.1	4.497	103.2
		11.010	88.8	—	—	9.334	102.3
„ benzylamide * ..	155.5	$c=4.855$	101.1	—	—	$c=4.654$	63.0
„ piperidide	157.5	0.5981	55.2	4.975	73.7	3.575	+38.5
		—	—	8.845	73.6	6.531	+40.5
„ phenylhydrazide	214	5.119	54.1	—	—	0.735	-129.8
		7.175	55.0	—	—	—	—

* McCrae (*loc. cit.*). In the case of the *n*-propylamide prepared by McCrae, our results corroborate those obtained by this author with pyridine solution, but our values, given in this table, for the glacial acetic acid solution of the *n*-propylamide are substantially higher than his, $[M]_D^{19^{\circ}} -101.3^{\circ}$, $c=4.798$. The temperatures at which McCrae's determinations were made were 20° for maldi-amide in glacial acetic acid, 17° in pyridine; 22° for the dibenzylamide in glacial acetic acid, and 15° in pyridine solution.

From the above table it will be seen how greatly the rotation is influenced by the solvent. Thus the alkylamides have a lower levorotation in pyridine than in methyl alcohol or glacial acetic acid; on the other hand, the benzylamide and the aromatic amides have a higher levorotation in pyridine than in glacial acetic acid solution. Again, whilst in the normal series of alkylamides in pyridine solution the levorotation is almost unaffected in passing from the methylamide to the *n*-heptylamide, in methyl alcohol there is a slight rise, and in glacial acetic acid solution a distinct decline in the molecular rotation. The derivatives of malamide in this respect exhibit much less regularity than those of tartramide (compare Frankland and Twiss), for in the latter series there is a continuous rise in the molecular rotation from the methyl to the heptyl term in the normal series in pyridine, and probably also in methyl alcohol and in water solution.

In both the malic and the tartaric series the rotation of the normal- is greater than that of the *iso*-propylamide, whilst the relative magnitudes of the rotation of the normal- and *iso*-butylamides in both series is dependent on the solvents, but in pyridine solution the *isobutylamide*, both malic and tartaric, has a higher rotation than the normal butylamide.

In both the malic and the tartaric series, the allylamide has a markedly lower molecular rotation, in all solvents, than the normal propylamide, thus showing that the presence of a double bond has not the invariable effect of increasing the optical activity as is often supposed.

Malic benzylamide, in pyridine solution, has a higher molecular rotation than the *n*-heptylamide in the same solvent, whilst in glacial acetic acid the relations are reversed. On the other hand, in pyridine solution, the molecular rotation of tartaric benzylamide is slightly inferior to that of the *n*-heptylamide.

The tartaric piperidide in pyridine solution is practically inactive, and therefore enormously less active than the *n*-heptylamide; similarly, the malic piperidide, in pyridine and in the methyl alcohol, is much less active than the *n*-heptylamide, although still strongly levorotatory; in glacial acetic acid the difference is greatly further emphasised inasmuch as the piperidide is strongly dextrorotatory.

The phenylhydrazide, again, in both malic and tartaric series, has in pyridine solution a much lower molecular rotation than the *n*-heptylamide, but in glacial acetic acid solution malic diphenylhydrazide has a higher rotation than the heptylamide. We have also found that the rotation of tartaric diphenylhydrazide is much greater in glacial acetic acid than in pyridine solution (see Frankland and Twiss).

In both malic and tartaric series, again, the aromatic amides have a much higher molecular rotation than the alkylamides.

E X P E R I M E N T A L.

Maldimethylamide.

Twelve grams of diethyl malate and 21 grams of absolute alcohol were placed in a tall cylindrical bottle immersed in ice. Methylamine was liberated from Kahlbaum's 33 per cent. aqueous solution by heat, passed through a lime drying-tube, and then into the above mixture. When 6 grams of methylamine had been thus passed in, the bottle was stoppered and allowed to stand for three days. On evaporating the alcohol a yield of 50 per cent. was obtained.

The methylamide is very soluble in hot or cold water, methyl alcohol, glacial acetic acid, methylated spirit, ethyl acetate, or pyridine, sparingly so in chloroform, benzene, or ether, and insoluble in carbon disulphide or light petroleum. From acetone it was obtained in acicular prisms and plates melting at 99°.

0.1047 gave 15.4 c.c. moist nitrogen at 11° and 762 mm. $N = 17.60$.

$C_6H_{12}O_3N_2$ requires $N = 17.50$ per cent.

Rotation of Maldimethylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
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Pyridine Solution.

4.634	0.987	1.9984	-5.12°	-56.01°	-89.6°
10.080	1.001	1.9984	11.35	56.27	90.0

Methyl Alcohol Solution.

6.250	0.8143	1.9984	-6.97°	-68.50°	-109.6°
9.982	0.8280	1.9984	11.14	67.42	107.9

Glacial Acetic Acid Solution.

4.267	1.060	1.9984	-6.83°	-75.54°	-120.9°
8.185	1.070	1.9984	12.83	73.26	117.2

Maldiethylamide.

Seven grams of ethylamine (Kahlbaum) in the form of vapour were passed into a mixture of 11 grams of diethyl malate and 13 grams of absolute alcohol cooled with a freezing mixture. On standing for some days in a stoppered bottle, the whole set into a solid mass of fine white, silky needles. Yield 90 per cent.

The ethylamide is very soluble in hot or cold water, methylated spirit, chloroform, pyridine, methyl alcohol, ethyl acetate, light petroleum, or

carbon disulphide. From benzene it was obtained as white, shining plates and needles melting at 122° .

0.1067 gave 14.0 c.c. moist nitrogen at 12° and 735.1 mm. $N = 15.05$.

$C_8H_{16}O_3N_2$ requires $N = 14.89$ per cent.

Rotation of Maldiethylamide.

<i>p.</i>	<i>d</i> $20^{\circ}/4^{\circ}$.	<i>l.</i>	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
4.319	0.9854	1.9984	-4.10°	-48.19	-90.6
10.250	0.9947	1.9984	9.66	47.41	89.1

Pyridine Solution.

Methyl Alcohol Solution.

4.984	0.8054	1.9984	-4.71°	-58.69	-110.3°
9.177	0.8185	1.9984	8.93	59.47	111.8

Glacial Acetic Acid Solution.

4.170	1.056	1.9984	-5.43°	-61.70°	-116.0°
7.995	1.060	1.9984	10.56	62.34	117.2

Maldi-n-propylamide.

Twelve grams of diethylmalate were added to 8 grams of *n*-propylamine (Kahlbaum), heat being evolved on mixing. On standing overnight the mixture had become almost solid. Yield 75 per cent. In order to obtain a theoretical yield, it is necessary to allow the mixture to stand for several days, or to heat on a warm water-bath for some hours.

The propylamide (m. p. 126°) is very soluble in water, benzene, alcohol, ethyl acetate, chloroform, pyridine, methyl alcohol, or glacial acetic acid, but insoluble in light petroleum or ether. It was purified by crystallisation from a mixture of benzene and light petroleum.

Rotation of Maldi-n-propylamide.

<i>n.</i>	<i>d</i> $20^{\circ}/4^{\circ}$.	<i>l.</i>	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
4.530	0.9833	1.9984	-3.73°	-41.90°	-90.5°
7.896	0.9895	1.9984	6.42	41.11	88.8

Methyl Alcohol Solution.

5.020	0.8061	1.9984	-4.28°	-52.91°	-114.3°
11.340	0.8260	1.9984	9.94	53.10	114.7

Glacial Acetic Acid Solution.

4.278	1.053	1.9984	-4.81°	-53.43°	-115.4°
5.040	1.052	1.9984	5.63	53.14	114.8
9.048	1.055	1.9984	9.96	52.20	112.8

Maldiisopropylamide.

10.7 grams of diethylmalate were added to a solution of 5.8 grams of isopropylamine (Kahlbaum) in 8.4 grams of absolute alcohol, but the reaction takes place so slowly in the cold that even after five weeks only a small quantity of the amide had crystallised out. The mixture was therefore heated in a stoppered bottle in a steam oven for six days. The yield was only 20 per cent. The substance is very soluble in hot water, alcohol, ether, acetic acid, pyridine, methyl alcohol, benzene, ethyl acetate, or acetone, but crystallises from each of these solutions on cooling. It is insoluble in light petroleum, and only very slightly soluble in carbon disulphide. It crystallises from acetone in long, slender needles melting at 150—151°.

0.1355 gave 15.7 c.c. moist nitrogen at 15° and 738.4 mm. $N = 13.17$.

$C_{10}H_{20}O_3N_2$ requires $N = 12.96$ per cent.

Rotation of Maldiisopropylamide.

ρ .	$d\ 20^\circ/4^\circ$.	l .	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
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Pyridine Solution.

2.548	0.9813	1.9984	-1.60°	-32.01°	-69.1°
3.986	0.9828	0.999	1.25	31.93	69.0

Methyl Alcohol Solution.

3.803	0.8035	1.9984	-2.60°	-42.57°	-92.0°
6.039	0.8091	0.999	2.04	41.79	90.3

Glacial Acetic Acid Solution.

3.710	1.050	0.999	-1.66°	-42.65°	-92.1°
6.284	1.056	0.999	2.84	42.83	92.5

Maldiallylamide.

11.1 grams of diethylmalate were mixed with 6.4 grams of allylamine (Kahlbaum) and 8.4 grams of absolute alcohol. Heat was developed on mixing, and, after standing for two days, a nucleus was obtained by placing a little of the mixture in a vacuum desiccator. On adding this nucleus to the remainder, and allowing to stand for a few days longer, a crop of pure white needles separated out from which the alcohol was evaporated. Yield 90 per cent. The allylamide is very soluble in hot or cold water, methyl alcohol, methylated spirit, ethyl acetate, chloroform, glacial acetic acid, or benzene. It is almost insoluble in light petroleum. From a mixture of benzene and light petroleum it was obtained in needles melting at 117.5°.

0.1438 gave 16.3 c.c. moist nitrogen at 12° and 752.8 mm. $N = 13.32$.

$C_{10}H_{16}O_3N_2$ requires $N = 13.21$ per cent.

Rotation of Maldi allylamide.

<i>n.</i>	<i>d</i> 20°/4.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
<i>Pyridine Solution.</i>					
4.639	0.9837	1.9984	-3.13°	-34.31°	-72.7°
10.390	0.9936	1.9984	7.20	34.89	74.0

Methyl Alcohol Solution.

4.804	0.8056	1.9984	-3.71°	-48.35°	-102.5°
9.095	0.8174	1.9984	7.24	48.72	103.3

Glacial Acetic Acid Solution.

4.492	1.060	1.9984	-3.90°	-40.99°	-86.9°
10.780	1.064	1.9984	9.45	41.22	87.4

Maldi-n-butylamide.

10.2 grams of diethyl malate were mixed with 7.8 grams of normal butylamine (Kahlbaum). Heat was developed on mixing, and, after standing overnight the whole had set solid. The mixture was allowed to stand for a few days longer. Yield 100 per cent.

The *n*-butylamide is very soluble in alcohol, ethyl acetate, benzene, or chloroform, insoluble in light petroleum or cold water, but soluble in hot water. It was obtained from dilute alcohol in shining, silver-white plates melting at 125°.

0.2278 gave 22.8 c.c. moist nitrogen at 12° and 746.7 mm. N = 11.67.

C₁₂H₂₄O₃N₂ requires N = 11.48 per cent.

Rotation of Maldi-n-butylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
<i>Pyridine Solution.</i>					
3.776	0.9804	1.9984	-2.64°	-35.68°	-87.1°
10.850	0.9860	1.9984	7.56	35.35	86.3

Methyl Alcohol Solution.

5.633	0.8037	1.9984	-4.32°	-47.74°	-116.5°
10.540	0.8160	1.9984	7.89	45.90	112.0

Glacial Acetic Acid Solution.

5.455	1.052	1.9984	-5.00°	-43.59°	-106.4°
9.718	1.052	1.9984	8.79	43.01	104.9

Maldiisobutylamide.

Ten grams of ethyl malate were added to 10 grams of *isobutylamine* (Kahlbaum), a little heat being evolved on mixing. After standing for a day and then warming on a water-bath for two hours, the mixture became solid, and a theoretical yield was obtained. The product is very soluble in hot water, ethyl or methyl alcohols, acetone, ethyl acetate, benzene, chloroform, ether, glacial acetic acid, or pyridine. It was crystallised from a mixture of benzene and light petroleum. Melting point 121° .

0.1456 gave 14.5 c.c. moist nitrogen at 14.5° and 755.8 mm. $N = 11.63$.

$C_{12}H_{24}O_3N_2$ requires $N = 11.48$ per cent.

Rotation of Maldiisobutylamide.

<i>p.</i>	<i>d</i> $20^{\circ}/4^{\circ}$.	<i>l.</i>	$\alpha_D^{20^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
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Pyridine Solution.

5.394	0.9813	1.9984	-3.77°	-35.63°	-86.9°
7.984	0.9837	1.9984	5.75	36.64	89.4

Methyl Alcohol Solution.

5.316	0.8039	1.9984	-4.11°	-48.11°	-117.4°
9.128	0.8153	1.9984	7.22	48.53	118.4

Glacial Acetic Acid Solution.

5.492	1.051	1.9984	-5.02°	-43.51°	-106.2°
7.563	1.051	1.9984	6.87	43.25	105.3

Maldi-n-heptylamide.

Sixteen grams of *n*-heptylamine (Kahlbaum) were added to 10 grams of diethyl malate, the mixture being accompanied by heat evolution. On standing overnight the whole had set to a solid mass. Yield 100 per cent.

The *n*-heptylamide is very soluble in hot alcohol, chloroform, pyridine, glacial acetic acid, or methyl alcohol, readily so in hot benzene or ethyl acetate. It is sparingly soluble in carbon disulphide, acetone, ether, or hot water. From methylated spirit it was obtained in beautiful white, shining plates melting at 130.5 — 131° .

0.2083 gave 15.6 c.c. moist nitrogen at 12.5° and 746.5 mm. $N = 8.71$.

$C_{18}H_{36}O_3N_2$ requires $N = 8.54$ per cent.

Rotation of Maldi-n-heptylamide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
<i>Pyridine Solution.</i>					
5.166	0.9792	1.9984	-2.73°	-27.01°	-88.6°
11.010	0.9804	1.9984	5.84	27.08	88.8

Methyl Alcohol Solution.

6.001	0.8035	1.9984	-3.41°	-35.38°	-116.1°
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A 10 per cent. solution crystallised.

Glacial Acetic Acid Solution.

4.497	1.050	1.9984	-2.97°	-31.47°	-103.2°
9.334	1.053	1.9984	6.13	31.20	102.3

Maldipiperidide.

Twelve grams of piperidine (Kahlbaum) were added to 10 grams of diethyl malate, and, although heat was evolved on mixing, only a 20 per cent. yield was obtained, even after keeping the mixture at 130° in an oil-bath for three days. A 50 per cent. yield was obtained by heating a similar mixture to the same temperature for ten days. The progress of the reaction is indicated by the contents of the flask becoming more and more solid on cooling. An attempt to prepare the piperidide by heating piperidine and malic acid together for several days proved unsuccessful.

The piperidide is very soluble in methylated spirit, but sparingly so in water, benzene, ethyl acetate, or pyridine. From a mixture of alcohol and acetone it was obtained in flat plates melting at 157.5°.

0.126 gave 11.2 c.c. moist nitrogen at 13° and 749.5 mm. $N = 10.35$.

$C_{14}H_{24}O_3N_2$ requires $N = 10.45$ per cent.

Rotation of Maldipiperidide.

<i>p.</i>	<i>d</i> 20°/4°.	<i>l.</i>	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
<i>Pyridine Solution.</i>					
0.5981	0.9794	3.899	-0.47°	-20.58°	-55.2°
<i>Methyl Alcohol Solution.</i>					
4.975	0.8078	1.9984	-2.21°	-27.51°	-73.7°
8.845	0.8200	0.999	1.99	27.47	73.6

Glacial Acetic Acid Solution.

3.575	1.061	1.9984	+1.09°	+14.37°	+38.5°
6.531	1.067	0.999	1.05	15.08	40.5

Maldiphenylhydrazide.

This compound was prepared, firstly, by Bülow's method (*Annalen*, 1886, 236, 194), which involves the use of a high temperature ($120-140^{\circ}$), and secondly, by Fischer and Passmore's method (*Ber.*, 1889, 22, 2734), in which the reaction is carried out on the water-bath. As will be seen below, however, the products obtained by both methods were of substantially the same rotatory power, thus showing that the higher temperature does not lead to any racemisation.

Bülow's Method.—Twenty-eight grams of phenyl hydrazine (Kahlbaum) were added to 20 grams of finely powdered malic acid; the mixture which solidified with evolution of much heat was further heated to $120-140^{\circ}$ for eight hours until no more steam was evolved. The heating must be begun with caution as there is a sudden evolution of a large amount of steam. The resulting mass, which was of a light brown colour, was first well washed with dilute acetic acid, and then with a solution of ammonium carbonate. The yield was 85 per cent. The substance is almost insoluble in water, methyl alcohol, or light petroleum, sparingly soluble in methylated spirit, and only slightly so in acetone, chloroform, carbon disulphide, ethyl acetate, ether, glacial acetic acid, or pyridine. It was obtained from alcohol in white shining plates melting at 214° with slight decomposition.

0.1232 gave 18.4 c.c. moist nitrogen at 11° and 764.2 mm. $N = 17.91$.

$C_{16}H_{18}O_3N_4$ requires $N = 17.83$ per cent.

Fischer and Passmore's Method.—Twenty grams of dried malic acid were dissolved in 180 grams of water, and to this were added a solution of 22 grams of glacial acetic acid in 22 grams of water with 40 grams of phenylhydrazine, the whole being then heated on the water-bath in a flask provided with an air-condenser. The reaction took place suddenly after heating for 4 hours, much of the liquid being violently projected into the condenser. The light brown product was washed successively with water, dilute acetic acid, and ammonium carbonate solution. The yield was only 20 per cent. The product had to be crystallised three times from glacial acetic acid before being obtained in a state of chemical and optical purity. Melting point 214° .

Rotation of Maldiiphenylhydrazide.

ρ .	$d\ 20^\circ/4^\circ$.	l .	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
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Pyridine Solution.

Preparation by	{	5.119	0.9929	1.9984	-1.75°	-17.22°	-54.1°
Bülow's method.	{	7.175	0.9987	1.9984	2.51	17.53	55.0
Preparation by	{	4.809	0.9914	1.9984	-1.65°	-17.28°	-54.3°
Fischer and Passmore's method.	{	6.390	0.9960	1.9984	2.17	17.06	53.6

Glacial Acetic Acid Solution.

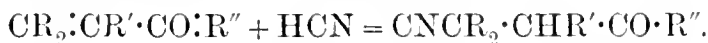
ρ .	$d\ 20^\circ/4^\circ$.	l .	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
0.7350	1.054	0.999	-0.32°	-41.35°	-129.8°

CHEMICAL DEPARTMENT,
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CLXXXI.—*Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part VI. The Action of Potassium Cyanide on Pulegone.*

By REGINALD W. L. CLARKE and ARTHUR LAPWORTH.

THE action of hydrogen cyanide in presence of bases or of potassium cyanide on $\alpha\beta$ -unsaturated ketones leads in all instances hitherto examined to the formation of a β -cyanoketone :

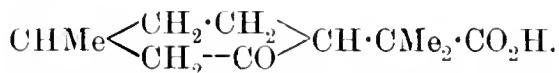


In the case of pulegone, reaction occurs somewhat slowly at the ordinary temperature, but if the ketone is heated on the water-bath with alcoholic potassium cyanide, a product is obtained which has the composition of the expected addition compound, the change being represented by the equation :



The substance, which was first referred to in a note by Hann and Lapworth (Proc., 1904, 20, 54), behaves in some respects as would the normal addition product, namely, cyanodihydropulegone (cyanomenthone), and was for a long time supposed to be that compound. In accordance with this supposition, it could be hydrolysed by acids

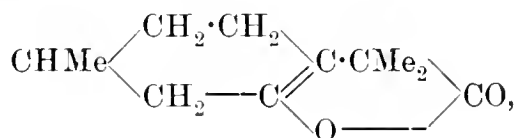
or alkalis, being converted into a saturated ketonic acid, namely, menthonecarboxylic acid,



Nevertheless, the supposed cyanoketone exhibited many characters mainly negative in type, which distinguished it from the others previously examined. Thus it did not react with hydrazines, semicarbazide, or hydroxylamine, and could not be made to yield a cyanohydrin. When boiled with alkalis, even in presence of ferrous hydroxide, no decomposition into pulegone and hydrogen cyanide could be detected, although β -cyanoketones as a rule are easily decomposed in this manner. The inactivity of the compound was suspected to be due to a manifestation of steric hindrance, although later a difficulty arose in applying this assumption, for the ketonic acid, to which it gave rise, reacted readily enough with the hydrazines and with hydrogen cyanide.

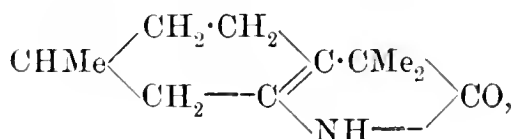
The clue to the character of the substance was finally obtained in the following manner.

Menthonecarboxylic acid is converted with great readiness into an unsaturated lactone,



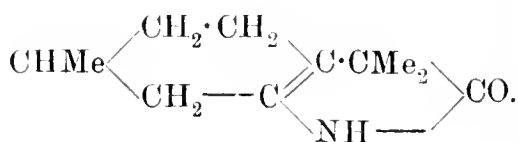
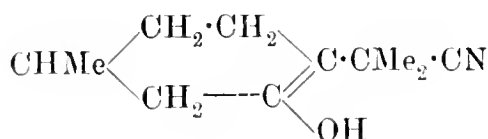
when warmed with mineral acids or when treated with acetyl chloride. This compound is precisely analogous in type to the anhydride obtained by Vorländer (*Annalen*, 1906, **345**, 188) from "pulegoneacetic acid," of which the present substance is the next lower homologue.

When the anhydro-derivative of menthonecarboxylic acid is shaken with ammonia, it yields a mixture of substances from which, by fractional crystallisation, a compound having the formula $\text{C}_{11}\text{H}_{17}\text{ON}$, and identical in all respects with the nitrogenous compound obtained by the action of potassium cyanide on pulegone, is obtained. To this substance, therefore, must be assigned the constitution

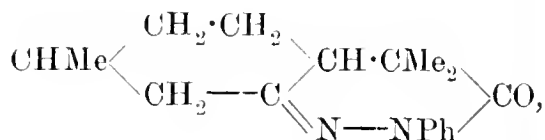
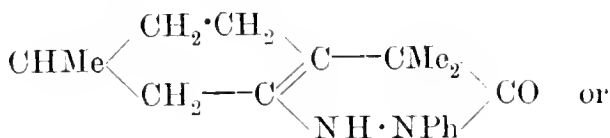


and is referred to in the paper as an "anhydramide," as it may be regarded as formed by the dehydration of menthonecarboxylic amide.

hydroxide, was without action; at higher temperatures hydrogen cyanide could be removed, but the product was always the anhydramide. By heating the cyanohydrin alone at its melting point, hydrogen cyanide is eliminated, but, again, the cyanomenthone at first produced at once undergoes isomeric change, and the anhydramide is the only substance which can be isolated. In the latter instance, it seems clear that the change must be represented as the result of the conversion of the cyanomenthone into its enolic form, in which the new ring formation then takes place,

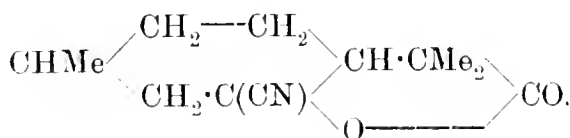


Although menthonecarboxylic acid could not be reduced by zinc and acetic acid, sodium amalgam, or sodium and ethyl or amyl alcohol, it exhibits most of the usual characters of a γ -ketonic acid, and reacts readily with phenylhydrazine, yielding the ring compound



which is the most characteristic derivative of the acid yet obtained; the oxime and semicarbazide are difficult to obtain in a pure state.

In presence of potassium cyanide, it is converted into a mixture of isomeric cyanolactones:

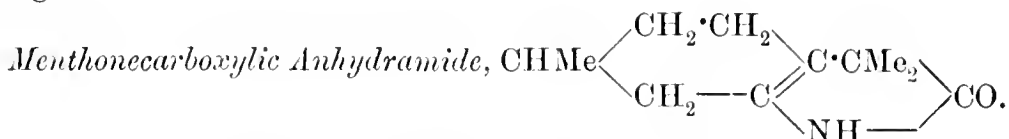


EXPERIMENTAL.

When pulegone is left in a cold solution of potassium cyanide in dilute alcohol it slowly absorbs hydrogen cyanide, and at the end of a week at the summer temperature is partially converted into cyanomenthonecyanohydrin. At 80—100° a mixture of this compound

with menthonecarboxylic acid, the anhydride of menthonecarboxylic amide, and the lactame of aminomenthonedicarboxylic acid is formed.

The relative proportion of the products obtained varies very greatly with the conditions used, and directions are given in the following pages for the preparation of each of the four compounds directly from pulegone.



—A solution of pulegone (45 grams) in 96 per cent. alcohol (75 c.c.) is mixed with a solution of potassium cyanide (25 grams) in water (30 c.c.) and the whole heated on the water-bath under a reflux condenser; at the end of about half an hour one molecular proportion of acetic acid, or, better, ethyl acetate, is slowly introduced beneath the surface of the liquid. The liquid, which at first forms two layers, gradually becomes homogeneous, and at the end of a further half hour is cooled and poured into a large bulk of water, when an oil is deposited which slowly becomes semi-solid. The average yield of the dried solid obtained from the above quantities was 45 grams. The product may be purified by fusing it in a round bottomed flask for ten minutes, a process which serves to convert any cyanomenthonecyanohydrin present into anhydramide, after which crystallisation from alcohol yields the pure anhydramide without difficulty. With large quantities of crude material, it is probably simpler to decompose the cyanohydrin present by boiling the material with a little alcoholic potash instead of fusing it.

0.2052 gave 0.5521 CO_2 and 0.1726 H_2O . $\text{C} = 73.4$; $\text{H} = 9.3$.

0.1703 „ 11.8 c.c. of moist nitrogen at 19° and 757 mm. $\text{N} = 7.9$.

$\text{C}_{11}\text{H}_{17}\text{ON}$ requires $\text{C} = 73.7$; $\text{H} = 9.5$; $\text{N} = 7.8$ per cent.

Menthonecarboxylic anhydramide is readily soluble in cold ethyl acetate, ethyl or methyl alcohols, chloroform, benzene, or acetic acid, and also in hot carbon disulphide, acetone, or ether, but is only sparingly dissolved by hot light petroleum or water.

The crystals are translucent needles which have straight extinction in polarised light, their directions of greatest length and elasticity being at right angles. The fused substance sets on cooling somewhat rapidly in long needles separated by air spaces, and when these are examined in convergent polarised light the acute bisectrix of a biaxial figure of narrow axial angle is sometimes seen to emerge nearly perpendicularly to the field. The dispersion is weak and the double refraction strong and negative in sign.

For the determination of its optical activity, 0.2515 gram dissolved

and made up to 25 c.c. with absolute alcohol was examined in a 2-dm. tube at 17°; the observed rotation was +1.34°, whence $[\alpha]_D + 66.6$.

This compound, which was for a long time thought to be cyanomenthone itself, is quite different in character from all the other β -cyanoketones. Thus, when it is heated with alcoholic potassium or sodium hydroxide containing ferrous hydroxide, it does not yield a trace of ferrocyanide, and pulegone is not obtained from it by this process. Further, it does not evince any tendency to react with hydrazines, with semicarbazide, or hydroxylamine; it does not yield a cyanohydrin with hydrogen and potassium cyanides, and is hardly affected by amyl nitrite or ethyl oxalate and cold sodium ethoxide.

The anhydramide behaves as an unsaturated compound, and when shaken with a cold solution of potassium permanganate, decolorises the liquid at once; its solution in acetic acid readily absorbs bromine even in presence of excess of sodium acetate (compare *Trans.*, 1904, 85, 38).

By the action of phosphorus pentachloride at 100° it is slowly converted with evolution of hydrogen chloride into a dark red substance. This gave a small quantity of oil when distilled, but it was not chlorocyanomenthene as was anticipated, for it was found to contain much phosphorus. The anhydramide dissolves in cold, strong sulphuric acid without change, is slowly hydrolysed by hot, strong hydrochloric or hydrobromic acid, and somewhat rapidly by alcoholic potassium hydroxide, in each case menthonecarboxylic acid being the main organic product.

Menthonecarboxylic acid, $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$, may be obtained from the anhydramide by the methods already mentioned, but it is more convenient to prepare it directly from pulegone by the same method as was recommended for preparing the anhydramide, but no acetic acid or ethyl acetate is added, and the heating is continued for four to five hours, after which the bulk of the alcohol is removed by distillation. The residue is diluted with water and poured into excess of dilute hydrochloric acid.

After standing for twenty-four hours, the insoluble matter which has separated is collected, washed with water, then extracted with benzene, which leaves undissolved the nitrogenous acid (p. 1879) formed at the same time, and the filtered benzene solution is extracted with dilute caustic soda solution, from which the ketonic acid is subsequently recovered by acidification. The compound is crystallised, first from dilute acetic acid, and, finally, from ethyl acetate. On analysis:

0.2002 gave 0.4864 CO_2 and 0.1636 H_2O . C = 66.5; H = 9.0.

$\text{C}_{11}\text{H}_{18}\text{O}_3$ requires C = 66.7; H = 9.1 per cent.

On titration with sodium hydroxide, 0.1962 of the acid required 10.0 c.c. of *N*/10 alkali for neutralisation, whence the equivalent of the compound was 196.2, whilst the number calculated for a monobasic acid, $C_{11}H_{18}O_3$, is 198.

Menthonecarboxylic acid dissolves readily in methyl or ethyl alcohols, acetone, benzene, chloroform, ether, acetic acid, or ethyl acetate, and sparingly in water and light petroleum. It separates from ethyl acetate in rosettes of small needles, which melt at 120—121°. Under the microscope, the needles are seen to be flattened, and in polarised light show straight extinction, and the relative directions of greatest length and elasticity vary according to the orientation of the crystal examined. After fusion, it solidifies slowly to opaque masses of very small quadrangular plates or elongated needles.

For the determination of its optical activity, 0.2500 gram dissolved and made up to 25 c.c. with absolute alcohol was examined in a 2-dm. tube. The rotation observed was -0.46° , whence $[\alpha]_D - 23.0$.

The compound behaves as a saturated ketonic acid, and when dissolved in sodium carbonate solution does not at once decolorise a cold solution of potassium permanganate; its solution in acetic acid does not decolorise bromine if sodium acetate is present.

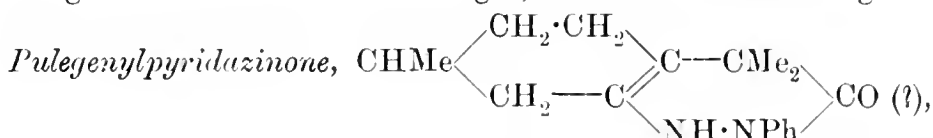
It is very stable towards reducing agents, and all attempts to convert it into the corresponding hydroxy-acid were unsuccessful. It did not appear to be affected by sodium amalgam, zinc dust, and acetic acid, stannous chloride in hot alkalis or cold acids, and even after attempted reduction with sodium and boiling ethyl or amyl alcohols was recovered almost unchanged. Attempts to reduce it by any agent in the presence of mineral acid resulted in the production of the anhydride mentioned later.

The *semicarbazone*, $C_{10}H_{18}O_2 \cdot N_2H \cdot CO \cdot NH_2$, was prepared by the usual method and purified by crystallisation from hot methyl alcohol, employing a Soxhlet extractor.

0.1049 gave 15 c.c. moist nitrogen at 18° and 759 mm. $N = 16.4$.

$C_{12}H_{21}O_3N_3$ requires $N = 16.5$ per cent.

It is sparingly soluble in methyl or ethyl alcohol, chloroform, acetone, ethyl acetate, benzene, carbon disulphide, or carbon tetrachloride. It separates from boiling methyl alcohol in small needles melting at 188° with evolution of gas, but without darkening.



is formed when the ketonic acid is heated with phenylhydrazine acetate, and usually crystallises when the product is washed with acid. It is purified by crystallisation from alcohol.

the neutral substance being extracted with ether. The dried ethereal extract is then fractionated at the ordinary pressure and the portion boiling at 245—247° cooled in a freezing mixture. The crystals which separated were drained on cold, porous earthenware and analysed :

0.2124 gave 0.5661 CO₂ and 0.1702 H₂O. C = 72.7 ; H = 8.9.

C₁₁H₁₆O₂ requires C = 73.3 ; H = 8.8 per cent.

The anhydride forms massive transparent rhombs, often approaching a centimetre in length. It is readily soluble in the usual organic solvents, but is only recrystallised from them with much difficulty ; it melts at 17.5—18°. 0.2500 gram dissolved and made up to 25.2 c.c. with absolute alcohol, was examined in a 2-dm. tube at 18° ; the observed rotation was +1.46°, whence $[\alpha]_D +73.6$.

When shaken with cold, dilute alkalis, even in the fused state, it does not at once dissolve, but disappears at the end of some hours or days, according to the temperature of the air. It is also reconverted into the ketonic acid by long-continued contact with water.

The substance, which is somewhat volatile in steam, has a marked odour of cocoa-nuts, and this renders it easy to detect small quantities of the ketonic acid, as it is merely necessary to boil it with 20 per cent. sulphuric acid when the odour of the anhydride soon becomes noticeable.

It has the properties of an unsaturated compound, at once absorbing bromine even in presence of sodium acetate and acetic acid. When it is shaken with a cold solution of potassium permanganate, the colour of the latter is almost instantaneously discharged.

In the expectation that the anhydro-compound would readily be converted into the amide of menthonicarboxylic acid, a portion of the former was shaken with aqueous ammonia (sp. gr. = 0.880) until it was converted into a mass of white needles. These were collected, washed, and crystallised from alcohol. Analysis of a specimen dried at 100° gave the following result :

0.2034 gave 14.25 c.c. of moist nitrogen at 19° and 762 mm. N = 8.1.

C₁₁H₁₉O₂N requires N = 7.1.

C₁₁H₁₇ON ,, N = 7.8 per cent.

The compound was therefore an anhydride of the amide, and was finally identified with the substance previously regarded as cyanomenthone, obtained by the action of potassium cyanide on pulegone. It melts at 165°, alone or when mixed with the supposed cyanomenthone. When 0.2518 gram was dissolved and made up to 25.1 c.c. with absolute alcohol, and examined in a 2-dm. tube at 22°, a rotation of +1.34° was observed, whence $[\alpha]_D +67.0$.

Cyanomenthonecyanohydrin, $\text{CHMe} \begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CH}_2 \cdot \text{C}(\text{OH})(\text{CN}) \end{array} \text{CH} \cdot \text{CMe}_2 \cdot \text{CN}$.

—This compound was obtained on attempting to prepare cyanomenthone by the action of potassium cyanide on pulegone in the cold. The ketone, dissolved in a large bulk of alcohol, was mixed with an aqueous solution of potassium cyanide, the amount of water and alcohol being so regulated that the whole was a homogeneous liquid. The mixture was allowed to remain at the ordinary temperature for about a week, and afterwards worked up by diluting it with water, when the oil which separated gradually became semi-solid. The solid matter was freed from adherent pulegone either by spreading it on porous porcelain or removing the pulegone with a current of steam. It was found that the same product was obtained whatever proportions of potassium cyanide were used in the first instance. A certain quantity of the anhydramide already described was usually formed at the same time, but cyanomenthone itself was never detected.

The cyanohydrin was purified by crystallisation from ethyl alcohol. On analysis :

0.1438 gave 16.7 c.c. of moist nitrogen at 17° and 771 mm. $N = 13.6$.

$C_{12}H_{18}ON_2$ requires $N = 13.6$ per cent.

Cyanomenthonecyanohydrin is fairly soluble in cold ethyl or methyl alcohol, acetone, ethyl acetate, chloroform, or ether, readily so in the hot solvents, sparingly so in carbon disulphide or carbon tetrachloride, and is almost insoluble in light petroleum or water.

It melts somewhat indefinitely at 195—197°, and decomposes if heated to its melting point for a short time without blackening, hydrogen cyanide being evolved.

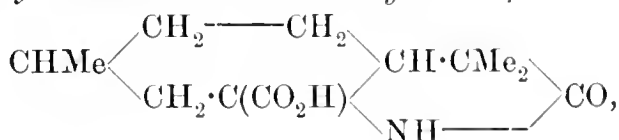
0.2606 gram dissolved in absolute alcohol and made up to 25.1 c.c., was examined in a 2-dm. tube at 16°; a rotation of -0.63° was observed, whence $[\alpha]_D - 30.3$. The crystals from alcohol are six-sided plates or elongated flat needles, having straight extinction in polarised light. The axial plane is identical with the plane of the larger faces of the crystals, but crushed fragments of the substance, examined in convergent polarised light, occasionally show the bisectrix of a figure of moderate axial angle. The double refraction is strong and positive in sign; the dispersion is weak.

The compound loses hydrogen cyanide readily and quantitatively at its melting point, and the residue sets to a mass of needles which, after recrystallisation, melted at 164—165°, and were identical with menthonicarboxylic anhydramide. At the ordinary temperature, however, the cyanohydrin exhibits a remarkable degree of stability, and is not decomposed by cold alcoholic potassium hydroxide even in presence of ferrous hydroxide, an agent which decomposes most cyanohydrins with great rapidity. No precipitate is formed when silver nitrate is added to the alcoholic solution, although cyanohydrins, as

a rule, are quantitatively decomposed by such treatment. When warmed with alcoholic alkalis in presence of ferrous hydroxide, the substance is decomposed and the ferrous hydroxide dissolves, but the product in all instances is the anhydramide and not cyanomenthone; the latter compound must be regarded as a very unstable one, being quickly converted into the anhydramide by heat or by the action of warm dilute alkalis.

The cyanohydrin is slowly converted by hydrochloric acid at 100° into the nitrogenous acid described below, but when heated with strong hydrobromic acid on the water-bath, it suffers more profound decomposition, and yields little but ammonium bromide and menthone-carboxylic acid after prolonged treatment.

The lactame of aminomenthane-dicarboxylic acid,



is produced in considerable quantities when pulegone is heated with potassium cyanide in dilute alcohol for several hours, and was therefore obtained in considerable quantities as a by-product in the preparation of menthonecarboxylic acid from pulegone. It was freed from attendant impurities by extracting it repeatedly with warm benzene and then recrystallising it from glacial acetic acid:

0.2454 gave 0.5751 CO₂ and 0.1860 H₂O. C = 63.9; H = 8.4.

0.1346 „ 7.7 c.c. moist nitrogen at 20° and 757 mm. N = 6.5.

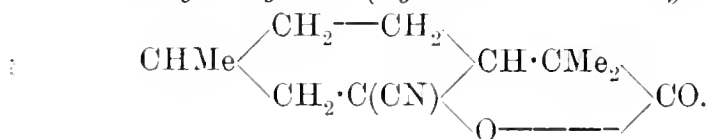
C₁₂H₁₉O₃N requires C = 64.0; H = 8.4; N = 6.2 per cent.

On titration with standard alkali, 0.3034 gram required 13.7 c.c. N/10 NaOH for complete neutralisation, the equivalent was therefore 222, whilst the number calculated for a monobasic acid of the above formula is 225.

This compound is very sparingly soluble in water, light petroleum, benzene, or chloroform, somewhat more readily so in alcohol, acetone, or ethyl acetate, but is freely dissolved only by glacial acetic acid. It separates from a hot solution in the latter solvent in small crystals melting at 237—239° after some preliminary sintering. Under the microscope, the substance presents the appearance of nodular aggregates of small needles, of which the optical characters could not be directly determined. The crystals obtained by fusing the substance between glass slips are transparent, well-formed needles, which slowly become opaque owing to contraction and consequent cracking; a part of the material often sublimes when heated, and the deposit consists of brilliant, well-formed, but minute plates, faceted in a complicated manner.

The substance is extremely stable and many attempts were made to convert it into hydroxymenthane-dicarboxylic acid or its lactone, but without success. It was not appreciably affected by strong boiling potassium hydroxide, hydrochloric acid, or dilute sulphuric acid. When dissolved in strong sulphuric acid to which sodium nitrite or amyl nitrite had been added, a slight change occurred on warming, but the greater portion of the material was recovered unchanged. Hypobromites or hypochlorites also had little or no effect at the temperature of the water-bath. When heated in a closed tube with fuming hydrochloric acid, no change was noticed at 120°, but after being heated to 170—180° for ten hours, the liquid separated into two layers, the upper one a dark brown oil. The whole was diluted with water and extracted with ether, and the ethereal solution shaken repeatedly with sodium hydroxide solution. On evaporation of the ether, a neutral oil remained. An attempt was made to distil this, but at 280° it evolved hydrogen chloride and the distillate had an odour of paraffin and peppermint, so that the original oil was probably a mixture of hydrochlorides of unsaturated ketones or of a hydrocarbon. The alkaline extract when acidified deposited an oil, which slowly solidified. After being drained on porous porcelain and crystallised from ethyl acetate it was obtained in needles melting at 122° and having all the characters of menthonecarboxylic acid.

Addition of Hydrogen Cyanide to Menthonecarboxylic Acid. Formation of Isomeric Cyanohydrins (Cyanomentholcarboxylactones),



—Menthonecarboxylic acid (1 mol.) dissolved in the requisite quantity of dilute sodium carbonate solution, was mixed with an aqueous solution of potassium cyanide (1½ mols.) in a flask which was afterwards closed with an india-rubber stopper, through which passed a dropping-funnel containing dilute sulphuric acid (1 mol.). A few c.c. of the sulphuric acid were allowed to run very slowly into the flask, which was then closed, and the addition of the remainder of the acid allowed to occur automatically (compare *Trans.*, 1906, 89, 964). At the end of twenty-four hours, the alkaline liquid was rendered slightly acid with sulphuric acid, the dark brown oil which separated being washed first with water, then with warm hydrochloric acid and finally extracted with petroleum. The petroleum solution was shaken with dilute sodium carbonate solution to remove acids, a process which caused the

separation of needles, but these dissolved on the addition of a little benzene. On evaporating the dried benzene-petroleum solution, a substance separated, which was purified by recrystallisation from light petroleum. On analysis :

0.1952 gave 0.4969 CO_2 and 0.1952 H_2O . $\% \text{C} = 69.9$; $\text{H} = 8.4$.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 69.6$; $\text{H} = 8.2$ per cent.

α -Cyanomentholcarboxylactone is readily soluble in all the usual organic media, and crystallises from light petroleum in slender needles melting at $48-49^\circ$.

The crystals are opaque needles, of which the optical properties are difficult to determine. When fused between glass slips, the substance sets to a mass of needles, through most of which a bisectrix of a narrow angled axial figure emerges obliquely. The double refraction is weak and positive in sign.

The compound is not acted on by cold aqueous alkali, but when boiled with aqueous sodium hydroxide dissolves, being converted into menthonecarboxylic acid and hydrogen cyanide. It is somewhat stable towards mineral acids, but when warmed with fuming hydrobromic acid yields ammonium bromide and menthonecarboxylic acid.

β -Cyanomentholcarboxylactone was obtained from that portion of the original oil which did not dissolve in light petroleum. It was isolated by dissolving the residue in benzene, shaking the resulting solution with sodium carbonate, and evaporating, the crystals which separated being purified by recrystallisation from a mixture of benzene and light petroleum. On analysis :

0.1845 gave 0.4683 CO_2 and 0.1371 H_2O . $\text{C} = 69.2$; $\text{H} = 8.3$.

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 69.6$; $\text{H} = 8.2$ per cent.

The substance is very readily dissolved by chloroform, benzene, or alcohol, somewhat readily also by ether or ethyl acetate, but is very sparingly soluble in light petroleum. It separates from a mixture of benzene and light petroleum in large, transparent crystals melting at $126-127^\circ$. The prisms are well formed, and in convergent polarised light some of these show the bisectrix of an axial figure of moderate angle. The double refraction is strong and negative in sign ; the dispersion is also fairly strong, the angle for blue light being greater than that for red. The axial plane is perpendicular to the direction of greatest length in the crystal. After fusion on a glass slide beneath a cover-slip, the lactone rapidly sets to patches of radiating or parallel needles, the optical properties of which were identical with those of the prisms just described.

In chemical properties the compound closely resembles the isomeric cyanolactone.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost of the investigation.

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CLXXXII.—*Note on the Anhydride of Phenylsuccinic Acid.*

By FRANK BERNHARD DEHN and JOCELYN FIELD THORPE.

THE anhydride of phenylsuccinic acid has been described as melting at 40—50° (Spiegel, *Annalen*, 1883, 219, 32), 53—54° (Alexander, *Annalen*, 1890, 258, 75), 150° (Bredt and Kallen, *Annalen*, 1896, 293, 347), and as existing in two forms, one melting at 53—54°, the other at 150° (Wegscheider and Hecht, *Monatsh.*, 1903, 24, 418). In spite of the fact that the compound melting at 150° was analysed and titrated by Bredt and Kallen, we are of the opinion that it is an impure form of the acid, and that phenylsuccinic anhydride exists in only one form, which melts at 53—54°.

The errors concerning the properties of this compound have evidently arisen owing to its remarkable instability in the presence of moisture. Thus it is apparently impossible to prepare the pure anhydride by distilling phenylsuccinic acid under diminished pressure, and although the distillate boils constantly, yet a considerable quantity of unchanged acid is always carried over by the anhydride vapour. The use of this method, both by Bredt and Kallen and by Wegscheider and Hecht, for the preparation of the anhydride accounts for the presence of unchanged acid in the products with which they worked. In the following experiments the experimental details given by these investigators have been closely followed.

Distillation of Phenylsuccinic Acid under Diminished Pressure.

The distillation of phenylsuccinic acid was conducted according to the directions given by Wegscheider and Hecht, about 50 grams of the acid being slowly distilled under a pressure of 16 mm. The distillate, which passed over constantly at 196°, solidified after standing

some hours and then melted at from 53—115°. A specimen of this product gave the following figures on analysis :

0.2012 gave 0.4892 CO₂ and 0.0856 H₂O. C = 66.31 ; H = 4.72.

C₁₀H₈O₃ requires C = 68.1 ; H = 4.5 per cent.

C₁₀H₁₀O₄ „ C = 61.8 ; H = 5.2 „

The solidified distillate was dissolved in dry ether and allowed to stand, when the characteristic crystals of phenylsuccinic anhydride slowly separated. The product melted sharply at 53—54°. Another portion of the same distillate was dissolved in hot xylene, which had previously been purified by distillation over sodium and the solution placed in a steam-heated oven for some days, when the solid which had then separated was isolated by filtration and washed with a little xylene. It melted at 150—153°, and gave the following result on analysis :

0.1984 gave 0.4500 CO₂ and 0.0991 H₂O ; C = 61.86 ; H = 5.55.

C₁₀H₁₀O₄ requires C = 61.8 ; H = 5.2 per cent.

The compound dissolved instantly in cold aqueous sodium carbonate with effervescence. Another portion of the distillate was placed in a test-tube, which after being sealed was placed in a steam-heated oven for several days. Crystals slowly separated, which, after the deposition had ceased, were isolated and found to melt at 150—156°.

The compound was instantly soluble in sodium carbonate solution with effervescence.

The products melting at 150—153° and 150—156° were recrystallised from hot, pure xylene, and in each case small needles melting at 168° separated from the solutions on cooling :

0.2083 gave 0.4722 CO₂ and 0.1037 H₂O ; C = 61.82 ; H = 5.53.

C₁₀H₁₀O₄ requires C = 61.8 ; H = 5.2 per cent.

This was evidently, therefore, pure phenylsuccinic acid.

Another portion of the solidified distillate melting at 53—115° was treated according to the method employed by Bredt and Kallen. It was thoroughly ground with cold light petroleum (b.p. 110—120°), and the solid residue, after being collected by filtration and washed with light petroleum, recrystallised from this solvent. The crystals which separated melted at 150—152° :

0.2078 gave 0.4713 CO₂ and 0.1015 H₂O. C = 61.85 ; H = 5.42.

C₁₀H₁₀O₄ requires C = 61.8 ; H = 5.2 per cent.

The compound dissolved in dilute aqueous sodium carbonate solution with effervescence, and, when recrystallised from xylene, yielded the pure acid melting at 168°.

Formation of Phenylsuccinic Anhydride from Phenylsuccinic Acid on Treatment with Acetic Anhydride and Subsequent Distillation.

Fifty grams of the acid were mixed with a large excess of freshly distilled acetic anhydride and heated on the sand-bath for five to six hours, when the acetic acid and unchanged acetic anhydride were distilled off, as far as possible, under the ordinary pressure and the residue distilled under a pressure of 16 mm. The anhydride passed over constantly at 196—197° as a colourless oil, which instantly solidified on cooling to a hard crystalline cake melting at 53—54°:

0.1976 gave 0.4923 CO₂ and 0.0821 H₂O. C = 67.94; H = 4.62.

C₁₀H₈O₃ requires C = 68.1; H = 4.5 per cent.

This anhydride, when dissolved in a little dried xylene and the solution placed in a steam-heated oven, deposited no solid even after three months. A portion sealed in a dried tube and also heated at 100° for the same period of time deposited no crystals, and another portion when sealed remained unchanged after standing three months at the ordinary temperature. Some of the anhydride was recrystallised from dry ether, and the large monoclinic crystals obtained in this way sealed in a tube which had been evacuated by the aid of the mercury pump. After three months, the surfaces of the crystals remained bright, and the melting point was found to be the same as before sealing. The anhydride also remained unaltered when kept either in an evacuated desiccator or in a sealed tube filled with dry air, but on exposure to the air of the laboratory it gradually passed into the acid, a change which was almost complete after three weeks (compare Hann and Lapworth, *Trans.*, 1904, 85, 1367).

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CLXXXIII.—*Studies in Optical Superposition. Part II.*

By THOMAS STEWART PATTERSON and JOHN KAYE.

IN the first part of this investigation (Patterson and Taylor, *Trans.*, 1905, 87, 33, 122), di-*l*-menthyl *d*-tartrate and its diacetyl derivative were described and data were given for their rotations, as well as for that of menthol, both in the homogeneous state and in solution. The present communication deals with the corresponding *l*-menthyl derivatives of *l*-tartaric acid.

In the first part, however, the chief problem for the elucidation of which the investigation was undertaken was not discussed, because the data secured were insufficient to supply a definite answer. The data which we now publish, whilst having, as in the former case, an interest of their own, are still insufficient to decide the main question at issue, but in consequence of the appearance of a paper by Rosanoff * (*J. Amer. Chem. Soc.*, 1906, 28, 525) we will state briefly here the ideas which we wish ultimately to test.

The rotation of a compound built up of two active radicles, for example, *d*-amyl *l*-lactate, may be regarded as the sum of two rotations, say α° and β° , one contributed by each radicle. van't Hoff is responsible for the assumption, very reasonable at the time it was made, that the rotation of *l*-amyl *l*-lactate may be represented as equal to $-\alpha^\circ + \beta^\circ$, a quantity obtained by merely reversing the sign of rotation of the amyl radicle. This assumption is known as the principle of optical superposition, and a considerable amount of experimental work has been undertaken by Guye and by Walden with the object of proving it.

A consideration of this work convinced us, firstly, that the experiments of Guye and Walden have in reality no bearing on the matter in hand, and, secondly, that the validity of van't Hoff's assumption is distinctly open to doubt.

According to a reference in Meyer and Jacobson's *Lehrbuch* (vol. i, 2nd edition, p. 104), Urban (*Arch. Pharm.*, 1904, 242, 51) has arrived at a similar conclusion, but unfortunately we have not been able to consult the original memoir. Lowry in a recent paper (*Trans.*, 1906, 89, 1039) also calls attention to a case in which van't Hoff's assumption is contradicted.

We may examine briefly an example of Walden's results. He prepared, for instance, three amyl lactates, and determined their rotations with the following results :

	$[\alpha]_D$	$[M]_D$
I. <i>i</i> -Amyl <i>l</i> -lactate.....	-6.38°	-10.21°
II. <i>l</i> -Amyl <i>i</i> -lactate.....	+2.64	+4.22
III. <i>l</i> -Amyl <i>l</i> -lactate.....	-3.93	-6.29

Since the sum of the molecular rotations of I and II (-5.99°) is nearly the same as the rotation of III (-6.29°), and from a number of other similar series of figures, Walden concludes that "die landesübliche Auffassung von der algebraischen Superposition der optischen Eigenschaften verschiedener asymmetrischen Kohlenstoffatome in einer Molekul findet ihre Bestätigung" (*Zeit. physikal. Chem.*, 1895, 17, 724). That is, the experiment quoted above is taken as proving that the rotation of the active lactyl radicle in I is the same as in III, the

* The paper has recently been republished in *Zeit. physikal. Chem.* 1906, 56, 565.

rotation of the active amyl radicle in II is the same as in III, and that therefore the rotation due to the lactyl radicle is the same whether it be combined with a *l*- or a *d*-amyl radicle.

It may be said at once that the mistake made here lies in regarding *i*-amyl and *i*-lactyl as simple radicles. The substances I and II above are not homogeneous compounds.* When *l*-lactic acid acts on *i*-amyl alcohol, two substances are formed—we may assume for the moment that they are formed in equal proportions—so that if small letters represent amyl radicles and capital letters represent lactyl radicles, we have

$$\text{I} = \begin{Bmatrix} d-L \\ l-L \end{Bmatrix} \quad \text{and} \quad \text{II} = \begin{Bmatrix} l-D \\ l-L \end{Bmatrix}.$$

Therefore, in supposing the rotation of I to be that of *i*-amyl *l*-lactate, Walden makes the tacit assumption that *l*-amyl and *d*-amyl have the same effect on the rotation of *l*-lactyl, the very point which was under investigation.

Further, of the four compounds composing I and II, *d*-*L* forming half of I and *l*-*D* forming half of II are enantiomorphs, so that their rotations would be equal and opposite, say, β° and $-\beta^\circ$, whilst the other half of I is the same as the other half of II. If, then, the pure compound *l*-*L* has a rotation equal to α° for a given length of tube, it is obvious that the rotation of I for the same length of tube will be equal to $\frac{1}{2}\alpha^\circ + \frac{1}{2}\beta^\circ$, whilst that of II will be equal to $\frac{1}{2}\alpha^\circ - \frac{1}{2}\beta^\circ$, their sum being, of course, α° , the rotation of the pure compound *l*-*L*.

What Walden has done in these cases, therefore, is merely to measure the rotation of *l*-*L* in two different ways, and it is not surprising that the results agree fairly closely. The experiments have been carried out in such a manner as to eliminate in each case the influence they were intended to discover.

There is, indeed, so far as we are aware, only one recorded instance in which this question can be directly tested, and, curiously enough, the data are supplied by Walden himself, who, however, makes no reference to their bearing on this particular subject. In a paper, "Ueber die optische Drehung stereoisomerer Verbindungen" (*Zeit. physikal. Chem.*, 1896, 20, 377), he gives values for the rotations of the di-*l*-amyl esters of racemic and *i*-tartaric acid, comparing them with the values for the rotations of the di-*l*-amyl esters of maleic and fumaric acid.

Now the *l*-amyl ester of racemic acid will, of course, consist of two non-enantiomorphic substances, and if we assume definite rotation

* This was clearly seen by Frankland and Price in the analogous case of the amyl glycerates (*Trans.*, 1897, 71, 267). These authors, however, were not thereby led to doubt the validity of van't Hoff's assumption. On the contrary, they accept it as the basis of some of their arguments.

values for the different active carbon atoms in these compounds according to the idea of van't Hoff, Guye, and Walden, we shall have, if $R = C_5H_{11} \cdot O \cdot CO-$

Di- <i>l</i> -amyl racemic ester.		Di- <i>l</i> -amyl <i>i</i> -tartaric ester.
I. (<i>dextro</i> -acid).	II. (<i>levo</i> -acid).	III.
(α°) R	(α°) R	(α°) R
(β°) H·C·OH	($-\beta^\circ$) HO·C·H	(β°) H·C·OH
(β°) HO·C·H	($-\beta^\circ$) H·C·OH	($-\beta^\circ$) H·C·OH
(α°) R	(α°) R	(α°) R
($2\alpha^\circ + 2\beta^\circ$).	($2\alpha^\circ - 2\beta^\circ$).	($2\alpha^\circ$).

Obviously the rotation of the racemic ester, since it is supposed to consist of equal parts of I and II, should be

$$= \frac{2\alpha^\circ + 2\beta^\circ}{2} + \frac{2\alpha^\circ - 2\beta^\circ}{2} = 2\alpha^\circ,$$

that is, should be the same as the rotation of the *i*-tartaric ester.

Walden's figures are :

	$[M]_D^{20^\circ}$.
Di- <i>l</i> -amyl <i>i</i> -tartrate	+13·83°
Di- <i>l</i> -amyl <i>dl</i> -tartrate	+ 9 77

Between these numbers there is a difference of 4·06°, almost half the rotation of the racemic ester, and much greater than the difference (0·3°) in the case of the amyl lactic esters already mentioned.

These data of Guye and Walden are not, however, experimentally sound. In all cases, as has been pointed out, the active compounds the rotations of which have been determined were mixtures, and herein lies a possible source of error. To take the last example quoted. When pure *l*-amyl alcohol acts on racemic acid, it is probable that the *d*- and *l*-acids do not esterify at the same rate, and since in the preparation of an ester the esterification is seldom or never complete, it is by no means unlikely that after distillation the resultant ester does not contain equal proportions of the *d*- and *l*-acid radicles. Further, the amyl alcohol used by Walden was itself also a mixture, which renders the experiment still more complicated and unreliable. The esterification of the *i*-acid would, of course, only be affected by the latter cause.

These considerations apply, however, to all the experiments with *l*-amyl alcohol and *dl*-acids, and therefore it might be expected that the experimental error in each series would be much the same. This is the case in all except the experiments with *i*-tartaric and racemic acid. The difference in the rotations of the esters of these acids can hardly be ascribed entirely to experimental error, and that

this difference has been found goes, we think, some way towards disproving van't Hoff's assumption.

In Rosanoff's paper, already referred to, the line of argument is exactly similar to ours,* and he arrives at the same conclusion, namely, that the "principle" of optical superposition is, at least, very doubtful.

He also suggests that in the experiments of Walden and of Guye solvent influence may exercise a disturbing effect. That this may be so is possible, but we are inclined to think that any solvent action which may come into play is likely to be of much less consequence than the possibility of selective esterification, mentioned above, which Rosanoff has overlooked.

One other point we may refer to. Rosanoff, in his paper (p. 529), in discussing a case of supposed optical superposition, says, "On the other hand, cases like Landolt's, if general instead of exceptional, would lead, not to the principle of optical superposition, but to the theorem that the rotatory power of an active radicle is independent of the chemical composition of the rest of the molecule," and to this passage he adds a footnote in the words: "Patterson and Taylor (Trans., 1905, 87, 33) seem to think that this is really what is meant by optical superposition."

It is difficult to understand how Rosanoff could have fallen into this error, since in the second paragraph of the paper to which he refers there occurs the passage, "When in a simple active molecule, such as that of lactic acid, the replaceable hydrogen atoms are substituted by radicles like methyl and ethyl or acetyl and benzoyl, the change in rotation which occurs with each substitution is probably due, not merely to the addition of a new group, but also to a modification, a slight molecular rearrangement of the active radicle itself. That is, the lactyl radicle, supposing it could be detached from a molecule of methyl lactate without suffering any other change, would show, when examined polarimetrically, a rotation differing from that of a lactyl radicle separated, in the same manner, from a molecule of some other lactate." The idea suggested here is surely the antithesis of the conception that the rotatory power of an active radicle is independent of the chemical composition of the rest of the molecule!

Rosanoff's paper contains no new experimental work, but some is promised, and, therefore, to prevent any possible overlapping we may state that the next part of this investigation will deal with the menthyl esters of *i*-tartaric acid, and we hope then to obtain data

* The foregoing, except for the references to more recent work, was written, in a more extended form, more than three years ago, and was intended to serve as an introduction to Part I of this investigation. For the reason given on p. 1885, however, it was omitted from that paper.

which shall supply a satisfactory solution to the problem of optical superposition.

EXPERIMENTAL.

The sodium ammonium *l*-tartrate used in this investigation was prepared by us from racemic acid.

That the salt was pure is shown by the following figures :

2.5 grams made up to 50 c.c. with water gave in a 2-dcm. tube the rotations :

<i>l.</i>	α_D		<i>l.</i>	α_D
16.3°	-4.650°		20.1°	-4.670°

from which $\alpha_D^{20} = -4.669$.

A recrystallised specimen of sodium ammonium *d*-tartrate, prepared from the dextro-acid, gave at the same concentration the figures :

<i>l.</i>	α_D		<i>l.</i>	α_D
13.9°	+4.62°		17.2°	+4.640°
16.9	4.634		22.5	4.669

from which $\alpha_D^{20} = +4.655$.

Di-l-menthyl-l-tartrate.—For the preparation of this substance it is not necessary to isolate *l*-tartaric acid from the sodium ammonium salt. The process used was as follows : some sodium ammonium tartrate was thoroughly dehydrated by heating in the steam bath for three to four hours. Fifty grams of the salt were placed in a round-bottomed flask with 158 grams of menthol, and dry hydrogen chloride was passed into the mixture, first in the cold and then at 110—130° for about twelve hours. The liquid mixture in the flask was then separated from the chlorides of sodium and ammonium formed, by pouring off while hot into a distilling flask. Most of the menthol was then distilled off under diminished pressure and steam blown through the viscid residue to remove the last traces. The ester in the flask was extracted with ether in which it did not seem very soluble, heating being necessary. A viscid brown solution was thus obtained, and on adding a small quantity of sodium carbonate solution (a few drops) a copious white precipitate separated. This, which proved to be sodium *l*-menthyl-*l*-tartrate, was filtered off and examined later. The ethereal extract was washed with sodium carbonate solution, then with water, and dried over anhydrous sodium sulphate. After removing the ether an attempt was made to distil the menthyl tartrate, but without success, as decomposition occurred. Attempts were also made to crystallise the ester after it had been purified by boiling, in ethyl alcoholic solution, with animal charcoal and then precipitating with water, but these were for a long time unsuccessful. Finally, we found that if the ester was dissolved in pyridine and water added, a crystalline substance

separated out. This compound, which contains pyridine, was recrystallised twice from light petroleum, when it melted at $69-70^{\circ}$.* We then found that if the menthyl tartrate was dissolved in light petroleum and a crystal of the above substance added, menthyl tartrate crystallised in fine needles melting at 42° . It was recrystallised from light petroleum, when it melted at the same temperature as before, and on analysis

0.1900 gave 0.4719 CO_2 and 0.1711 H_2O . $\text{C} = 67.73$; $\text{H} = 10.00$.

$\text{C}_{22}\text{H}_{42}\text{O}_6$ requires $\text{H} = 9.86$; $\text{C} = 67.61$ per cent.

We made two attempts to determine the rotation of this ester, one with a specimen prepared before we had obtained any in the crystalline condition, and therefore purified by precipitation with water from ethyl alcoholic solution, and another with the crystallised substance. Since in both cases we observed the same behaviour we need quote only from the latter. The substance was melted and poured into a 30 mm. tube. It did not crystallise on cooling, so the first rotation was taken at $t: 16.3^{\circ}$, when $\alpha_D - 23.86^{\circ}$. On raising the temperature the rotation increased, and at 134.9° had the value $\alpha_D - 24.12^{\circ}$. On the following morning, however, the rotation had not returned to the original value, but at 18.4° , $\alpha_D - 24.31^{\circ}$, and a day or two later at 130° , $\alpha_D - 24.51^{\circ}$. On cooling again to 9.5° , α_D had become -24.69° , and when heated to 98.2° , $\alpha_D - 24.83^{\circ}$. The last observation made at 9.3° gave $\alpha_D - 24.77^{\circ}$, and at 99.3° α_D had the value -24.84° . These observations extended over about a fortnight; they show no constancy, but to what this is due we cannot explain.

The density of the menthyl tartrate was also determined twice. The results agreed closely, as is shown by the following figures: Series I was carried out with an oil purified by precipitation, Series II with the crystallised substance.

Series I.	Series II.	Density.	Series I.	Series II.	Density.
t .	t .		t	t .	
—	71.5°	1.0028	—	136°	0.9536
—	79	0.9968	137°	—	0.9541
94°	—	0.9866	--	154	0.9396
—	112	0.9725			

Obviously, specific and molecular rotations deduced from the above values are of little importance, but the following numbers for the extremes at low and at high temperatures may be given:—

t° .	α_D° (30 mm.).	Density.	$[\alpha]_D^{\circ}$.	$[M]_D^{\circ}$.
$\left\{ \begin{array}{l} 16.3^{\circ} \\ 9.3 \end{array} \right.$	$\left\{ \begin{array}{l} -23.86^{\circ} \\ 24.77 \end{array} \right.$	$\left\{ \begin{array}{l} 1.0450 \\ 1.0505 \end{array} \right.$	$\left\{ \begin{array}{l} -76.11^{\circ} \\ 78.60 \end{array} \right.$	$\left\{ \begin{array}{l} -324.2^{\circ} \\ 334.8 \end{array} \right.$
$\left\{ \begin{array}{l} 134.9 \\ 99.3 \end{array} \right.$	$\left\{ \begin{array}{l} 24.12 \\ 24.84 \end{array} \right.$	$\left\{ \begin{array}{l} 0.9547 \\ 0.9816 \end{array} \right.$	$\left\{ \begin{array}{l} 84.22 \\ 84.36 \end{array} \right.$	$\left\{ \begin{array}{l} 358.8 \\ 359.4 \end{array} \right.$

* This substance will be more fully investigated later.

Sodium l-Menthyl l-Tartrate.—As already mentioned (p. 1889), a substance was precipitated in rather a curious manner from the ethereal extract of crude menthyl tartrate on the addition of a drop or two of sodium carbonate solution. This compound was not very soluble in hot water. On cooling, the solution became turbid, and, on standing, clusters of needle-shaped crystals separated and the solution became quite clear. The substance was recrystallised from water. It did not melt when heated to 200° . On igniting with sulphuric acid:

1.0091 gave 0.208 Na_2SO_4 . $\text{Na} = 6.68$.

0.7013 „ 0.147 Na_2SO_4 . $\text{Na} = 6.79$.

0.3480, dried at 100° , lost 0.0191 H_2O . $\text{H}_2\text{O} = 5.48$.

$\text{C}_{14}\text{H}_{23}\text{O}_6\text{Na}, \text{H}_2\text{O}$ requires $\text{Na} = 7.01$; $\text{H}_2\text{O} = 5.48$ per cent.

The rotation of the compound was determined in aqueous solution with the following result:

<i>p.</i>	<i>t</i> °.	α_D^{20} (170 mm.).	Density.	$[\alpha]_D^{20}$.	$[\text{M}]_D^{20}$.
0.3623	48.6°	-0.466°	0.9896	-76.46°	-250.8°

Menthyl diacetyl-l-tartrate was prepared by boiling menthyl tartrate with excess of acetyl chloride for several hours. The residue, after the acetyl chloride had been distilled off, was washed with water and sodium carbonate solution, when it became solid. The compound, when dry, was dissolved in hot methyl alcohol and boiled under a reflux condenser with animal charcoal, the solution filtered and allowed to cool. The crystals which separated were recrystallised from aqueous methyl alcohol, when they melted at 102.5° . On analysis:

0.1947 gave 0.4705 CO_2 and 0.1558 H_2O . $\text{C} = 65.90$; $\text{H} = 8.89$.

0.2136 „ 0.5164 CO_2 „ 0.1711 H_2O . $\text{C} = 65.93$; $\text{H} = 8.90$.

$\text{C}_{28}\text{H}_{46}\text{O}_8$ requires $\text{C} = 65.88$; $\text{H} = 9.02$ per cent.

The molecular weight of the compound was determined cryoscopically in benzene solution ($K = 50$), the following data being obtained: Theoretical M.W. = 510.

Weight of substance.	Weight of solvent.	Grams or substance per 100 grams of solvent.	Δ .	M.W.
0.1903 gram	16.65 grams	1.14	0.11°	519.5
0.2863 „	16.65 „	1.72	0.17	505.7
0.4466 „	16.65 „	2.68	0.28	478.9
1.0580 „	17.15 „	6.17	0.67	460.4

In this case, therefore, as was also found for the corresponding derivative of *d*-tartaric acid (Patterson and Taylor, Trans., 1905, 87, 40), the molecular weight diminishes with increasing concentration, but the substance seems to be unimolecular in very dilute solution.

The rotation of the substance in the homogeneous condition was then determined with the following result. The ester remained super-cooled for a long time, and therefore the observations could be extended over a wide range of temperature. The numbers are recorded in the order in which they were obtained.

Rotation of Di-l-menthyl Diacetyl-l-tartrate.

t° .	α_D^t (30 mm.).	Density.	$[\alpha]_D^t$.	$[M]_D^t$.
122.5°	-22.135°	0.9697	-76.10°	-388.1°
129.0	22.080	0.9645	76.31	389.2
146.5	22.020	0.9505	77.23	393.9
104.5	22.195	0.9842	75.18	383.4
15.0	22.237	1.0558	70.21	358.1
49.3	22.204	1.0283	71.98	367.2
103.0	22.166	0.9853	75.00	382.5
150.0	22.042	0.9477	77.54	395.4
16.0	22.242	1.0550	70.28	358.4

Densities determined:

t°	98°	122°	142°
$d_{..}$	0.9894	0.9701	0.9541

There is no sign here that any permanent alteration of rotation had occurred.

The rotations of *l*-menthyl *l*-tartrate, and *l*-menthyl diacetyl *l*-tartrate were then determined in ethyl alcohol, benzene, and nitrobenzene with the following results:

l-Menthyl l-Tartrate.

Solvent: *Ethyl Alcohol.*

p .	t° .	Density.	α_D^t (170 mm.).	$[\alpha]_D^t$.	$[M]_D^t$.
I. 2.41729	14.25°	0.8009	-2.490°	-75.64°	-321.7°
	27.6	0.7893	2.491	76.77	327.0
	38.9	0.7779	2.493	77.90	331.8
	20.0 *	—	—	76.06 *	324.0 *
II. 7.05393	18.0°	0.8055	-7.29°	-75.48°	-321.5°
	24.6	0.8000	7.30	76.10	324.2
	48.0	0.7800	7.30	78.05	332.5
	20.0 *	—	—	75.60 *	322.2 *

Densities determined:

	t° .	d .		t° .	d .
I.	19.55°	0.79615	II.	18.25°	0.80516
	23.2	0.79305		22.95	0.80136
	29.8	0.78741		38.6	0.78766

* Interpolated.

l-Menthyl l-Tartrate (continued).Solvent: *Benzene*.

	<i>p.</i>	<i>t</i> °.	Density.	α_D^C (170 mm.).	$[\alpha]_D^C$.	$[M]_D^C$.
I.	2·73118	18·3°	0·8825	−3·001°	−73·22°	−311·9°
		31·0	0·8690	3·000	74·35	316·5
		38·0	0·8615	3·000	75·00	319·5
		20·0 *	—	—	73·33 *	312·4 *
II.	5·39447	15·1°	0·8890	−6·083°	−74·57°	−317·7°
		24·5	0·8790	6·071	75·30	320·8
		35·9	0·8670	6·065	76·34	325·2
		20·0 *	—	—	74·94 *	319·2 *

Densities determined:

	<i>t</i> °.	<i>d.</i>		<i>t</i> °.	<i>d.</i>
I.	18·5°	0·88196	II.	17·75°	0·88591
	21·5	0·87910		21·60	0·88202
	27·0	0·87342		30·15	0·87303

Solvent: *Nitrobenzene*.

	<i>p.</i>	<i>t</i> °.	Density.	α_D^t (170 mm.).	$[\alpha]_D^t$.	$[M]_D^t$.
I.	1·98411	13·8°	1·2047	−3·610°	−88·84°	−378·5°
		20·2	1·1983	3·600	89·06	379·4
		41·0	1·1775	3·528	88·87	378·5
		51·5	1·1667	3·483	88·43	376·7
		13·6	1·2049	3·619	89·08	379·5
		20·0 *	—	—	89·02 *	379·2 *
II.	5·34773	13·5°	1·1975	−9·727°	−89·37°	−380·7°
		25·3	1·1857	9·610	89·15	379·7
		31·3	1·1797	9·529	88·86	378·5
		42·0	1·1692	9·482	89·19	379·9
		20·0 *	—	—	89·32 *	380·5 *

Densities determined:

	<i>t</i> °.	<i>d.</i>		<i>t</i> °.	<i>d.</i>
I.	17·85°	1·20082	II.	17·50°	1·19337
	20·80	1·19783		29·75	1·18149
	29·30	1·18933		43·50	1·1679

l-Menthyl Diacetyl-l-tartrate.Solvent: *Ethyl Alcohol*.

	<i>p.</i>	<i>t</i> °.	Density.	α_D^t (170 mm.).	$[\alpha]_D^t$.	$[M]_D^t$.
I.	3·9479	20·2°	0·7985	−3·871°	−72·21°	−368·3°
		32·6	0·7879	3·874	73·18	373·3
		42·0	0·7795	3·874	73·97	377·2
		20·0 *	—	—	72·20 *	368·2 *
II.	5·80053	16·7°	0·8053	−5·675°	−71·52°	−364·7°
		26·8	0·7953	5·675	72·29	368·7
		38·0	0·7854	5·680	73·34	374·0
		20·0 *	—	—	71·77 *	366·0 *

* Interpolated.

1-Menthyl Diacetyl-1-tartrate (continued).

Densities determined:

	t° .	d .		t° .	d .
I.	21.0°	0.79799	II.	19.1°	0.80333
	25.5	0.79407		24.0	0.79895
	39.4	0.78200		37.2	0.78784

Solvent: *Benzene*.

	p .	t° .	Density.	$\alpha_D^{t^{\circ}}$ (170 mm.).	$[\alpha]_D^{t^{\circ}}$.	$[M]_D^{t^{\circ}}$.
I.	2.06209	21.0°	0.8795	-1.885°	-60.97°	-310.9°
		31.5	0.8685	1.895	62.08	316.6
		15.0	0.8860	1.895	60.85	310.3
		20.0 *	—	—	61.17 *	312.0 *
II.	5.21901	15.3°	0.8905	-4.822°	-61.01°	-311.1°
		27.5	0.8775	4.827	62.01	316.2
		20.0 *	—	—	61.37 *	313.0 *

Densities determined:

	t° .	d .		t° .	d .
I.	17.75°	0.88319	II.	17.85°	0.88769
	21.25	0.87941		20.87	0.88450
	30.50	0.86930		30.10	0.87483

Solvent: *Nitrobenzene*.

	p .	t° .	Density.	$\alpha_D^{t^{\circ}}$ (170 mm.).	$[\alpha]_D^{t^{\circ}}$.	$[M]_D^{t^{\circ}}$.
I.	2.59034	16.8°	1.2016	-3.710°	-70.09°	-357.5°
		28.8	1.1898	3.698	70.56	359.8
		58.1	1.1610	3.666	71.68	365.5
		20.0 *	—	—	70.06 *	357.3 *
II.	5.35741	15.3°	1.1935	-7.570°	-69.36°	-353.7
		29.8	1.1842	7.568	70.18	357.9
		44.0	1.1704	7.546	70.80	361.0
		20.0 *	—	—	69.54 *	354.7 *

Densities determined:

	t° .	d .		t° .	d .
I.	16.66°	1.20187	II.	17.75°	1.19594
	22.80	1.19579		21.42	1.19231
	32.80	1.18594		30.65	1.1833
				48.4	1.1661

* Interpolated.

The table below is a synopsis of these data. In it are given the rotation values (by interpolation) of the various active compounds examined in 5 per cent. solutions in ethyl alcohol, benzene, and nitrobenzene. We think it better to give these values rather than numbers for infinitely dilute solution, since, perhaps, for purposes of comparison

it is preferable to deal with concentrations which can be practically realised.

Condition.	<i>l</i> -Menthyl <i>d</i> -tartrate. <i>l</i> -Menthyl <i>l</i> -tartrate.		Δ .
	$[\text{M}]_D^{20^\circ}$.	$[\text{M}]_D^{20^\circ}$.	
Homogeneous	-284.0°	-325.0° (?)	41.0°
In ethyl alcohol (5 per cent.)...	305.1	323.0	17.9
„ benzene „ ...	293.6	318.4	24.8
„ nitrobenzene „ ...	246.0	380.4	134.4

	<i>l</i> -Menthyl diacetyl- <i>l</i> -Menthyl diacetyl-		
	<i>d</i> -tartrate.	<i>l</i> -tartrate.	
Homogeneous	-256.4°	-359.6°	103.2°
In ethyl alcohol (5 per cent.)...	268.2	367.0	98.8
„ benzene „ ...	285.0	312.9	27.9
„ nitrobenzene „ ...	238.0	355.1	117.1

The chief point of interest which we find in these data is that the differences between the rotations of the corresponding *d*- and *l*-compounds, under these different conditions or in solution, are not constant. Thus, for example, solution in benzene increases the negative rotation of *l*-menthyl diacetyl-*d*-tartrate by 28.6°, whilst it diminishes that of *l*-menthyl diacetyl-*l*-tartrate by 46.7°, so that whereas the difference in the rotations of the homogeneous compounds as given in the Δ -column is 103.2°, in benzene solution it is only 27.9°. In ethyl alcohol solution the rotations of both acetyl tartrates are increased, but that of the dextro- to a greater extent than that of the lævo-compound. In nitrobenzene the opposite is the case: both rotations are diminished, that of the dextro-compound to the greater extent. The behaviour in each of these three cases is different, and the fourth possibility is found in the behaviour of *l*-menthyl *d*- and *l*-tartrates in nitrobenzene, the rotation of the former being diminished by 38° and that of the latter increased by about 55°.

It is not difficult to understand this if we assume that the solvent exerts its influence separately on each of the three active groups of which the molecule is composed, and that our measurements represent the sum of these effects. Thus the influence of a solvent on the menthyl part of *l*-menthyl diacetyl-*d*-tartrate will probably be the same, or much the same, as its action on the menthyl radicle of *l*-menthyl diacetyl-*l*-tartrate, whilst its influences on the tartaryl parts of the molecules will probably be equal, or almost equal, but in opposite senses. If, then, the solvent influence is represented by $\alpha + \beta$ in one case, it will be represented by $\alpha - \beta$ (or nearly) in the other, and it will depend on the relative magnitudes of α and β for different solvents which of the four possible cases exemplified above shall occur.

It is also possible to trace other approximately additive phenomena somewhat similar to those discussed in Part I. (pp. 38, 39) when we consider the change of rotation of these compounds with variation of

temperature. The numbers for menthyl diacetyl *d*- and *l*-tartrates at 100° and 0° are the following :

<i>t</i> °.	<i>l</i> -Menthyl diacetyl- <i>d</i> -tartrate.		<i>l</i> -Menthyl diacetyl- <i>l</i> -tartrate.	
	$[M]_D^C$.	Δ .	$[M]_D^C$.	Δ .
100°	-227·6°	39·2°	-381·8°	-27·8°
0	266·8		354·0	

The rotation of the *d*-tartrate is diminished (that is, becomes less negative) by 39·2° on heating from 0° to 100°. This corresponds with the behaviour of ethyl diacetyl-*d*-tartrate the positive rotation of which increases on heating (Patterson and McCrae, Trans., 1900, 77, 1098). The rotation of the *l*-menthyl diacetyl-*l*-tartrate, on the other hand, increases by 27·8° (that is, becomes more negative). Since these changes are in opposite directions it seems reasonable to suppose that they are chiefly due to those parts of the molecules which are of opposite configurations, namely, the acetyl-tartaryl radicles, and that the numerical difference between them, 11·4°, represents twice the change of rotation of two menthyl radicles attached to an acetyl-tartaryl radicle on heating from 0° to 100°. Thus, of the total change in rotation (39·2°) of the dextro-compound, +33·5° are due to the acetyl-*d*-tartaryl part of the molecule, and +2·85° to each of the menthyl radicles, all these changes being in the same direction, whilst in the lævo-compound the total change of rotation (-27·8) is made up of -33·5, due to the acetyl-*l*-tartaryl group, and +5·7°, due to the two menthyl groups.

The independent effect of each active group in the molecule seems, therefore, to be, at least roughly, traceable, although, of course, the above argument ignores the possibility that the change in rotation of, say, a menthyl radicle might be different according to whether it were combined with a *d*- or *l*-acetyl-tartaryl group. It is likely, however, that such an influence would be slight, which is borne out to some extent by the fact that the change deduced above for a menthyl radicle attached to an acetyl-tartaryl group (2·85°) is in fair agreement with that actually observed in *l*-menthyl acetate (2·3°) which was discussed in Part I. (Trans., 1905, 87, 38).

We arrive at a somewhat similar conclusion from an examination of the variation of density of these compounds with change of temperature which the following data exhibit.

	<i>l</i> -Menthyl <i>d</i> -tartrate.		<i>l</i> -Menthyl <i>l</i> -tartrate.	
<i>t</i> °.	Density.	Δ.	Density.	Δ.
70°	1·0152	0·0617	1·0040	0·0610
150	0·9535		0·9430	
	<i>l</i> -Menthyl diacetyl- <i>d</i> -tartrate.		<i>l</i> -Menthyl diacetyl- <i>l</i> -tartrate.	
70°	1·0202	0·0640	1·0118	0·0641
150	0·9562		0·9477	

It will be seen from these numbers that the change of density due to rise of temperature from 70° to 150° has almost the same value for the two simple tartrates, namely, 0·0610 and 0·0617, and that the same holds for the acetyl derivatives for which the changes are 0·0641 and 0·0640, but the change for either of the simple tartrates is quite different from that for an acetyl derivative, compare for example 0·0610 and 0·0641.

From this we may conclude that the *l*-menthyl group expands to the same extent on heating, whether it be combined with a *d*- or a *l*-tartaryl radicle, and that the latter groups also expand to the same extent when combined with an *l*-menthyl radicle. All these changes must of course be in the same sense, and differ in this respect from the corresponding rotation changes.

So far we have dealt with variation of density; we may now consider the actual densities of the substances examined. Taking values at 100° we have

Substance.	Density.	Δ .	Substance.	Density.	Δ .
<i>l</i> -Menthyl <i>d</i> -tartrate	0·9922	0·0111	<i>l</i> -Menthyl diacetyl- <i>d</i> -tartrate	0·9962	0·0085
<i>l</i> -Menthyl <i>l</i> -tartrate	0·9811		<i>l</i> -Menthyl diacetyl- <i>l</i> -tartrate	0·9877	

Between the densities of the simple esters there is a difference of 0·0111, and between those of the acetyl derivatives a difference of 0·0085.

On the other hand, the difference in density between *l*-menthyl *d*-tartrate and *l*-menthyl diacetyl-*d*-tartrate is only 0·0040, whilst the difference in density between the corresponding lævo-compounds is 0·0066. *Thus there is a greater difference in density between the two simple tartrates than exists between one of these and its acetyl derivative.* The difference in density caused by mere spatial change of the groups composing the molecules is distinctly greater in both cases than that due to a considerable difference of chemical composition.

This difference between two compounds which differ only spatially is perhaps shown more clearly in their molecular volumes.

Substance.	M. V. ^{100°} .	Δ .
<i>l</i> -Menthyl <i>d</i> -tartrate	429·3 c.c.	4·9 c.c.
<i>l</i> -Menthyl <i>l</i> -tartrate	434·2 „	
<i>l</i> -Menthyl diacetyl- <i>d</i> -tartrate	512·0 c.c.	4·4 c.c.
<i>l</i> -Menthyl diacetyl- <i>l</i> -tartrate	516·4 „	

The volume change due to re-arrangement is greater in the smaller than in the larger molecule.

We have also calculated, from our density determinations, values for the solution volumes of these two compounds in the various solvents used. We should mention, however, that owing to scarcity of material the data were obtained (except in the case of *l*-menthyl diacetyl-*l*-tartrate in nitrobenzene) with a pyknometer having a capacity of only 7 c.c. The values for M.S.V. are therefore probably not so accurate as those formerly given for the corresponding derivatives of *d*-tartaric acid. The values, at both concentrations examined, for the diacetyl-*l*-tartrate in ethyl alcohol and benzene agree fairly closely and therefore confirm each other. The values for the same substance in nitrobenzene are the most reliable of all, having been obtained with a larger pyknometer.

Molecular Solution Volumes.

l-Menthyl *l*-tartrate, $[M]_D^{20} = 325^\circ$ (?). $M.V.^{20} = 426/1.042 = 408.9$ c.c.

Solvent.	<i>p</i> .	<i>d</i> .	M.S.V. ²⁰ .	$[M]_D^{20}$.
Ethyl alcohol (δ $20^\circ/4^\circ = 0.79045$) ...	2.41729	0.79577	389.8* c.c.	- 324.0°
	7.05393	0.80393	410.8 „	322.2
Benzene (δ $20^\circ/4^\circ = 0.87784$)	2.73118	0.88053	431.0 c.c.	- 312.4°
	5.39447	0.88364	426.2 „	319.2
Nitrobenzene (δ $20^\circ/4^\circ = 1.20319$) ...	1.98411	1.19864	380.6* c.c.	- 379.2°
	5.34773	1.19095	422.1 „	380.5

* These values are doubtful.

l-Menthyl diacetyl-*l*-tartrate, $[M]_D^{20} = -359.6^\circ$.

$M.V.^{20} = 510/1.0518 = 484.9$ c.c.

	<i>p</i> .	<i>d</i> .	M.S.V. ²⁰ .	$[M]_D^{20}$.
Ethyl alcohol	3.9479	0.79887	472.9 c.c.	- 368.2°
	5.80053	0.80252	477.9 „	366.0
Benzene	2.06209	0.88076	487.5 c.c.	- 312.0°
	5.21901	0.88542	485.7 „	313.0
Nitrobenzene	2.59034	1.19856	487.1 c.c.	- 357.3°
	5.35741	1.19371	486.7 „	354.7

These numbers do not exhibit any simple relationship between solution volume and rotation, but from the table below it will be observed that in all cases except one the volume of the *l*-tartrate in solution is greater than that of the *d*-tartrate, which is, as has already been remarked, also the case for the compounds in the homogeneous state.

Solvent.	<i>l</i> -Menthyl <i>l</i> -tartrate.		<i>l</i> -Menthyl <i>d</i> -tartrate.		Δ .
	ρ .	M.S.V. ²⁰ .	ρ .	M.S.V. ²⁰ .	
Ethyl alcohol.....	7.1	410.8 c.c.	7.9	398.3 c.c.	+12.5 c.c.
Benzene	5.4	426.2 „	7.4	409.5 „	+16.7 „
Nitrobenzene.....	5.3	422.1 „	6.5	408.2 „	+13.9 „
	<i>l</i> -Menthyl diacetyl- <i>l</i> -tartrate.		<i>l</i> -Menthyl diacetyl- <i>d</i> -tartrate.		
	ρ .	M.S.V. ²⁰ .	ρ .	M.S.V. ²⁰ .	
Ethyl alcohol....	5.8	477.9 c.c.	7.3	480.0 c.c.	-2.1 c.c.
Benzene	5.2	485.7 „	7.8	482.5 „	+3.2 „
Nitrobenzene.....	5.4	486.7 „	6.3	483.0 „	+3.7 „

* Trans., 1905, 87, 124—126.

That the molecular volumes or molecular solution-volumes of partial enantiomorphs, like those we have been dealing with, should be different is by no means remarkable. It is merely in agreement with the very well-known fact that the solubility of compounds such, for instance, as cinchonine-*d*- and *l*-tartrate or mannose, glucose and galactose is different, and it is further in agreement with the fact that such substances differ also in melting point. The melting points of the substances examined in this investigation, for example, are as follows:—

<i>l</i> -Menthyl <i>d</i> -tartrate	74—75°	<i>l</i> -Menthyl diacetyl- <i>d</i> -tartrate...	$\left\{ \begin{array}{l} 84.5^\circ * \\ 108.0 \end{array} \right.$
<i>l</i> -Menthyl <i>l</i> -tartrate	42	<i>l</i> -Menthyl diacetyl- <i>l</i> -tartrate...	102.5

* The substance is dimorphous.

From the fact that when an active group A_l combines respectively with two other enantiomorphic groups, B_d and B_l , the changes in the reacting groups, which accompany combination, are not the same in the two cases, since the melting points, solubility and density of the resulting substances are different, and, in spite of the fact that, on the other hand, the variation of volume and, so far as we can judge, the variation of rotation of the group A_l , with change of temperature seem to be independent of the configuration of the other group with which it is combined, it is scarcely to be expected that the rotation of such partially enantiomorphic substances should be a purely additive property.

As has been said, however, there exist no unimpeachable data to settle the question, but we hope with the next part of this investigation to produce some evidence of a decisive character.

It gives us pleasure, in conclusion, to acknowledge our indebtedness to the Research Fund Committees of the Chemical Society and of the Royal Society for grants which defrayed the expenses of this investigation.

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CLXXXIV.—*The Interaction of the Alkylsulphates with the Nitrites of the Alkali Metals and Metals of the Alkaline Earths.*

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As silver nitrite by its interaction with the alkyl iodides yields a nitro-compound as well as an ester, it has often been taken for granted that this nitrite has a twofold constitution, namely, nitronic and oxylic. Evidence has already been adduced in favour of the latter structure (Rây and Gaṅguli, *Proc.*, 1905, 21, 278), which Dr. Divers is inclined to accept as fairly conclusive (*ibid.*, p. 281). It seemed to us that further light would be thrown on the question by studying the reaction between the alkylsulphates and the alkali nitrites, as the latter have always been supposed to have the oxylic constitution.

EXPERIMENTAL.

I. *Potassium Ethylsulphate and Sodium Nitrite.*

Lauterbach has published a brief note on the subject (*Ber.*, 1878, 11, 1225), but a systematic investigation seemed desirable, especially as this chemist contented himself with demonstrating the formation of ethyl nitrite by its odour and inflammability, and also in view of the additional interest lent to the subject by Wade's fruitful research on the interaction between the alkylsulphates and potassium cyanide (*Trans.*, 1902, 81, 1596).

Dried and powdered potassium ethylsulphate and sodium nitrite were mixed in molecular proportions in a glass retort, to the neck of which was attached an inverted condenser. The upper end of the condenser was connected with a bulb provided with stop-cocks at both ends and three absorption bottles containing 90 per cent. alcohol. As the temperature of the laboratory was about 30°, the entire condensation and absorption apparatus was immersed in ice-cold water. It will be seen below that even this arrangement failed to condense the whole of the ethyl nitrite, as during the reaction a constant stream of nitric oxide was evolved, which carried off a considerable amount of it. For the same reason the air was expelled by a slow stream of carbon dioxide. The retort was heated in a glycerol bath. The reaction, which commences at 145°, is indicated by frothing, which slowly extends towards the centre from the peripheral regions. When the reaction once begins it proceeds continually, even when the temperature sinks so low as 110°. After a certain interval, the action becomes very violent and a

sudden and vigorous evolution of white vapours takes place. The reaction then moderates, effervescence ceases, and the mass has the appearance of tranquil fusion. The digestion lasts from two and a half to three hours.

(a) *Ethyl Nitrite.*

Although it is "dry" ethylsulphate which is heated, much alcohol is given off at the temperature at which the reaction takes place (compare Wade, *loc. cit.*). A portion of this alcohol is carried off and condensed with ethyl nitrite in the bulb. The alcoholic solution of the ethyl nitrite in the bulb, as also in the absorption bottles, was estimated according to the method prescribed in the British Pharmacopœia. As will be shown below, the result is somewhat too low owing to the fact that a part of the nitrite escapes condensation, being carried off with the stream of nitric oxide and carbon dioxide.

(b) *Nitroethane.*

The nitroethane was now distilled off, using a small condenser, the distillation being continued as long as oily drops appeared. The distillate was shaken up with brine and the oily layer separated, washed with water, and dried over calcium chloride. Considerable difficulty was experienced here, as it was found that calcium chloride forms with the "oil" a kind of emulsion. When our work was at this stage, Wade's paper on "The Influence of Water and Alcohols on the Boiling Point of Esters" (Trans., 1905, 87, 1656) appeared, which materially helped us. Fused sodium sulphate was used as the dehydrating agent, as potassium carbonate acts on nitroethane. When the "oil" was subjected to distillation, curious and anomalous behaviour was noticed. A considerable amount passed over below 100° ; only a small fraction could be collected at a constant boiling point between 110° and 118° , whilst a minute quantity came over between 150° and 160° and the residue charred. As pointed out by Wade (*loc. cit.*, 1668), an ethereal liquid containing alcohol, when shaken up with brine, does not give up its alcohol, but, on the contrary, "shares its alcohol with it." The fraction below 100° answered to all the well-known tests of nitroethane, namely, it solidified completely on the addition of alcoholic sodium hydroxide, and the aqueous solution of the sodium compound gave with ferric chloride a red coloration, and with copper sulphate a green precipitate. Obviously the quantity of nitroethane formed cannot be determined by fractionation.* Known mixtures of

* A mixture made up of 5 c.c. of alcohol and 5 c.c. of nitroethane, when shaken up with brine and dried over fused sodium sulphate, gave 6.1 c.c. of "oil" which, on fractionation, gave 4.5 c.c. distilling between 75° and 100° and only 1.3 c.c. between 100° and 115° .

nitroethane and alcohol were treated with alcoholic sodium hydroxide, the precipitate washed with absolute alcohol and ultimately converted into sodium sulphate and weighed as such; but the results turned out to be too low. Consequently the nitrogen in an aliquot portion of the liquid was estimated according to Dumas' method, and from it the amount of nitroethane in the mixture deduced. The fraction between 110° and 118° was nearly pure nitroethane. The results of 3 experiments out of 27 are given below, 32.8 grams of potassium ethylsulphate and 14 grams of sodium nitrite being taken in each case.

No. of experiment.	Weight of ethyl nitrite in grams.	Weight of nitroethane in grams.
1	2.3	1.3
2	3.2	1.0
3	2.0	1.3

As has been already explained, some of the ethyl nitrite is invariably lost, and the figures for nitroethane are also a little too low, as quite an appreciable quantity of it remains mixed with the liquid of higher boiling point (see below). The yield of nitroethane is 6 to 8 per cent. of that which is theoretically possible.

(c) *Liquid of Higher Boiling Point.*

The fraction which distilled at $150\text{--}160^{\circ}$ was very small, and not more than 0.15 gram could be recovered in each experiment. In order to study its nature and properties, the distillates from several preparations were mixed, and the crude "oil," after being treated with brine and fused sodium sulphate as above, was subjected to fractional distillation under diminished pressure in Brühl's apparatus. Four fractions were collected, namely, $40\text{--}60^{\circ}$, $60\text{--}65^{\circ}$, $65\text{--}125^{\circ}$, and $125\text{--}130^{\circ}$, the distillation taking place under a pressure of 130 mm. The ranges of temperature recorded above are only approximate; in fact, the liquid gave evidence of the properties of a homogeneous ternary mixture (compare Wade, *loc. cit.*). Blank experiments showed that pure nitroethane distilled at $63\text{--}65^{\circ}$ under the above pressure, so that the second fraction was nearly pure nitroethane. The fraction $125\text{--}130^{\circ}$ proved to be α -nitro-*n*-butane with traces of a compound of a still higher boiling point. The analyses of two typical samples of different preparations are given below:

I. C = 47.06; H = 8.23; N = 14.10.

II.* C = 46.06; H = 6.60; N = 13.85.

$\text{C}_4\text{H}_9\text{O}_2\text{N}$ requires C = 46.60; H = 8.73; N = 13.60 per cent.

* This represents a fraction which distilled at $150\text{--}160^{\circ}$ under the ordinary pressure.

The vapour density of the liquid was found by Hofmann's method to be 50.4, that required by nitrobutane being 51.50. That it has this constitution is evident from the fact that its boiling point was about 150°, and it gave with alcoholic sodium hydroxide the characteristic precipitate and with potassium hydroxide, on standing, a yellow deposit. It also responded to the nitrolic acid test.

II. *Potassium Ethylsulphate and Potassium Nitrite.*

The conditions of the experiment were similar to those previously described. The mass fused at a much higher temperature, namely, at about 165°, and the reaction proceeded without the aid of heat; white fumes and nitric oxide were evolved. The yield of nitroethane was much less than in the former experiment.

Expt. 1.—32.8 grams of potassium ethylsulphate and 17 grams of potassium nitrite gave 1.5 grams of ethyl nitrite and 0.8 gram of nitroethane. In this case also nitrobutane was formed, as will be seen below.

Expt. 2.—164 grams of potassium ethylsulphate and 85 grams of potassium nitrite yielded 8.5 c.c. of "oil" which on distillation under the ordinary pressure gave 70—100°, 5.0 c.c.; 100—150°, 1.5 c.c.; and 150—160°, 0.5 c.c.

III. *Barium Ethylsulphate and Barium Nitrite.*

Barium ethylsulphate crystallises with 2 molecules of water, and is completely dehydrated when kept for a few days over sulphuric acid under diminished pressure (see analysis given below), whilst the nitrite still retains some water (Rây, *Trans.*, 1905, **87**, 177). The anhydrous alkylsulphate and the nitrite were mixed in equimolecular proportions. The mass did not fuse and froth up, even when the temperature of the bath was raised to 190°. A distillate passed over which was mainly alcohol. With the hydrated salts, however, fusion commenced at 120°, but the action suddenly became violent at about 130°, and white fumes were evolved with violence. The yield of nitroethane was very poor, and only a few drops could be collected, which, however, answered to all the tests of this compound.

IV. *Calcium Ethylsulphate and Calcium Nitrite.*

Calcium ethylsulphate, which also crystallises with 2 molecules of water, is completely dehydrated, like the barium salt, when kept over sulphuric acid under diminished pressure. The anhydrous salt mixed with dehydrated calcium nitrite in equimolecular proportions does not fuse on heating, but simply decomposes when the temperature is

sufficiently raised. The hydrated salts were therefore used. The mixture fused at 116° , but at about 125° torrents of white fumes were evolved. The yield of nitroethane was again very poor, the last drops of the distillate responding to the reactions for this substance.

V. *Sodium Ethylsulphate and Sodium Nitrite.*

In the hope of obtaining better yields of nitroethane, the sodium salt was next tried. It crystallises with 1 molecule of water, which may be removed when kept under diminished pressure over sulphuric acid (see analysis given below). The anhydrous salt did not fuse with sodium nitrite, even when the temperature was raised to 195° . The hydrated salt, however, when similarly treated, began to fuse at so low a temperature as 80° , and the action, once begun, proceeded of itself as in the case of the potassium salt. The temperature of the bath was not allowed to rise above 120° . The sudden evolution of white fumes was never noticed. As the reaction takes place at a much lower temperature, it gave a better yield of nitroethane, and, moreover, the liquid having a higher boiling point was not formed. The results of the two experiments are given below, 33.2 grams of sodium ethylsulphate and 13.8 grams of sodium nitrite being taken in each case.

Expt. 1 gave 0.6 gram of ethyl nitrite and 2.2 grams of nitroethane. Expt. 2 gave 0.9 gram of ethyl nitrite and 2.0 grams of nitroethane. The yield of nitroethane is thus as much as 13 per cent. of the theoretical, whilst it is only about 6 to 8 per cent. when the potassium salt is used.

VI. *Sodium Ethylsulphate and Potassium Nitrite.*

This reaction began with frothing at a higher temperature than that in V, namely, at 120° when the hydrated salt was used, there being no fusion with the anhydrous salt. There was, again, no evolution of white fumes, and the reaction proceeded of itself when once started, nitrobutane not being formed. The yield of nitroethane is, however, much less, being almost equal to that obtained from potassium ethylsulphate and sodium nitrite. 33.2 grams of sodium ethylsulphate and 17 grams of potassium nitrite gave 0.9 gram of ethyl nitrite and 1.3 grams of nitroethane.

Conclusion.

The formation of nitrobutane, as noticed in I and II, is remarkable, and it is always associated with vigorous evolution of white fumes. Moreover, the interaction of sodium ethylsulphate and sodium nitrite,

which takes place at a much lower temperature, does not give rise to this compound. This mode of ascent in the homologous series does not admit of an easy explanation. The alcohol which was used in the present investigation was proved to be free from impurities. It was rectified over quicklime and had a constant boiling point (78°). The analyses of the various alkylsulphates are given below.*

The argument in favour of the twofold constitution of silver nitrite simply because it yields with ethyl iodide both ethyl nitrite and nitroethane is scarcely tenable. The alkali nitrites have the constitution $\text{MO}\cdot\text{NO}$, where M represents the atom of the metal, in other words, the nitrogen is not directly attached to it. Hence we should have only expected the production of ethyl nitrite in the present series of experiments, but its formation is always accompanied with that of its isomeride. The more correct view would seem to be that it is only during the substitution of the atom of the metal by the alkyl radicle that a tautomeric change takes place.†

Summary.

From the foregoing investigation, it would appear that by the interaction of the sodium, potassium, barium, and calcium salts of ethylsulphuric acid and the nitrites of the alkali metals and metals of the alkaline earths, both ethyl nitrite and nitroethane are formed. In the case of the potassium ethylsulphate and potassium or sodium nitrite small quantities of nitrobutane are also obtained.

PRESIDENCY COLLEGE,
CALCUTTA.

* $(\text{C}_2\text{H}_5\text{SO}_4)_2\text{Ba}\cdot 2\text{H}_2\text{O}$. Ba, found 32.79; calculated 32.70.

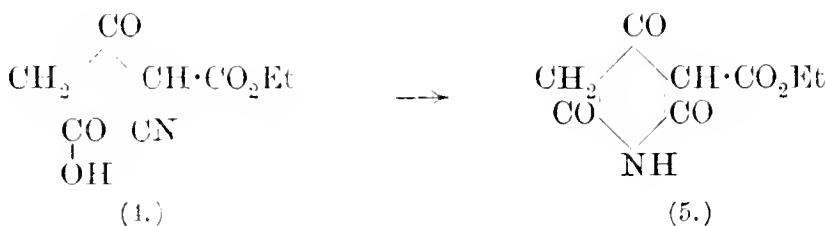
$(\text{C}_2\text{H}_5\text{SO}_4)_2\text{Ba}$. Ba, found 36.01 and 35.88; calculated 35.77.

$\text{C}_2\text{H}_5\text{NaSO}_4\cdot\text{H}_2\text{O}$. Na, found 13.70; calculated 13.85.

$\text{C}_2\text{H}_5\text{NaSO}_4$. Na, found 15.72; calculated 15.54 per cent.

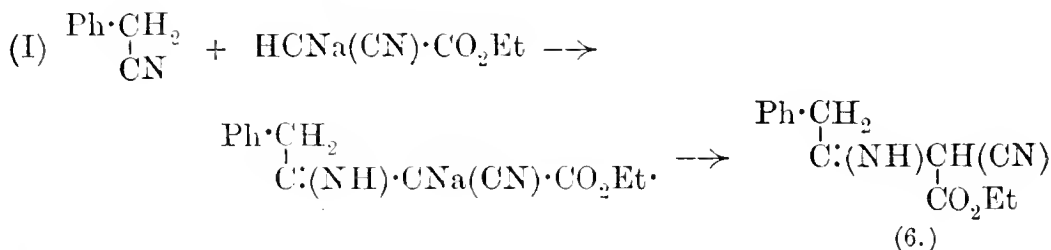
† Whether the hypothesis of tautomerism is adequate or not, there is evidently much force in what Wade urges: "It does not follow, for example, that because silver cyanate and nitrite yield alkylisocyanates and nitro-compounds respectively, the metal is necessarily linked to nitrogen; it may equally be linked to oxygen" (*loc. cit.*, p. 1612).

pyridine ring, which is indicated by this reaction, was still more strongly shown by the behaviour of ethyl hydrogen β -imino- α -cyano-glutarate (3), which was found to undergo conversion into ethyl glutazinecarboxylate (2) on being heated a few degrees above its melting point (*loc. cit.*, 1746). There seemed to be, therefore, a considerable tendency for a nitrile group in the γ -position to a carboxyl group in a compound such as ethyl hydrogen β -imino- α -cyanoglutarate to pass, by intermolecular change with that group, into a six-membered ring, and that this tendency is also shown by the corresponding β -ketonic derivatives was demonstrated by the conversion of ethyl hydrogen cyanoacetonedicarboxylate (4) into ethyl 2:4:6-trioxypyridine-3-carboxylate (5), on heating a few degrees above its melting point.

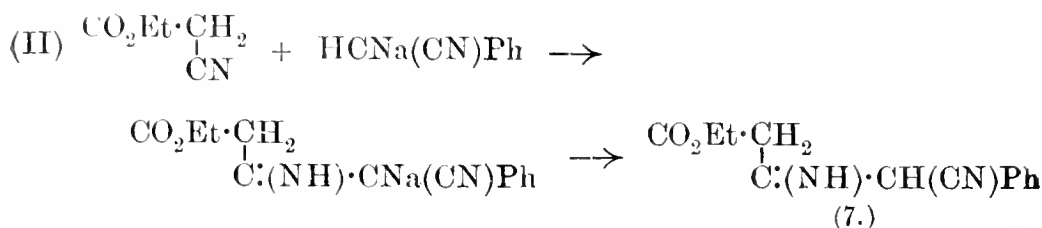


Whilst desiring to continue the investigation of the conditions of formation of these imino-compounds, we wished at the same time to ascertain whether the tendency of the nitrile group to enter into ring formation might not be applied to the formation of carbon rings as well as those containing nitrogen, and with this object in view and for other reasons which will be given later, we have investigated the condensation of benzyl cyanide with the sodium compound of ethyl cyanoacetate and also with its own sodium derivative.

It is apparent that the most probable course of the first reaction would be represented by the equation (I), and that the product on acidifying would be ethyl β -imino- α -cyano- γ -phenyl-*n*-butyrate (6).

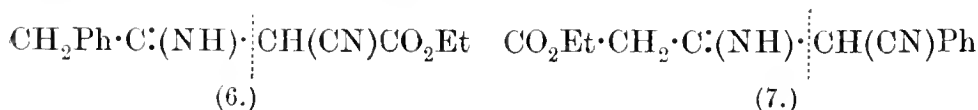


But it is also possible that the sodium derivative of ethyl cyanoacetate might react with benzyl cyanide, forming the sodium derivative of the latter, in which case the course of the condensation would be represented by equation (II), and on acidifying ethyl β -imino- γ -cyanophenyl-*n*-butyrate (7) would be the chief product.



Under conditions given in the experimental portion of this paper, a good yield of a well-defined crystalline compound (m. p. 125°) is formed on condensing benzyl cyanide with ethyl sodiocyanoacetate, and there can be no doubt that its constitution is represented by formula (6), although, under certain experimental conditions, there is evidence that a compound of formula (7) also occurs as an intermediate product.

In Part I. of this series (p. 1728), it was shown that β -imino-ethyl salts are decomposed on treatment with alkaline hydrolytic agents and that the products formed, which are the same as those derived by the alkaline hydrolysis of the corresponding β -keto-ethyl salts, often afford valuable evidence as to the formula of the compound hydrolysed. It is apparent, however, that this method fails when applied to two compounds of formulæ (6) and (7), since these two substances would yield the same products, namely, a mixture of malonic and phenylacetic acids, on complete hydrolysis, thus:

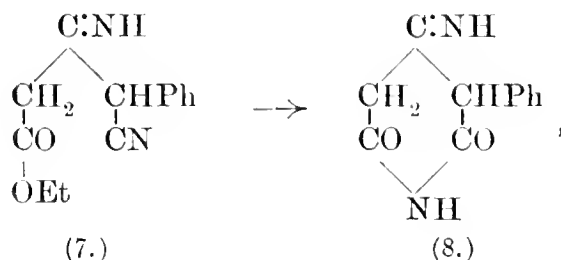


The compound melting at 125° is readily hydrolysed by means of an alcoholic solution of potash, and the product consists of about equal proportions of malonic and phenylacetic acids. Although by this means, therefore, it is not possible to distinguish between the two formulæ (6) and (7), yet the evidence is valuable, since, taken in conjunction with the boiling point of the compound (235°/20 mm.) and its percentage composition, it shows that it has been formed by the condensation of one molecule of benzyl cyanide with one molecule of ethyl cyanoacetate.

It was necessary, therefore, to adopt some other means of distinguishing between the two compounds of formulæ (6) and (7), and since we were unable to isolate any intermediate products during the alkaline hydrolysis, the formation of which might throw some light on the problem, we were led to study the action of concentrated sulphuric acid on the compound melting at 125°.

If the two formulæ are examined, it will be seen that the action of this reagent must give rise to different compounds.

A substance of formula (7) is closely allied to ethyl β -imino- α -cyanoglutarate (see page 1906) in constitution, and therefore should readily give phenylglutazine (8) on treatment with concentrated sulphuric acid, thus :

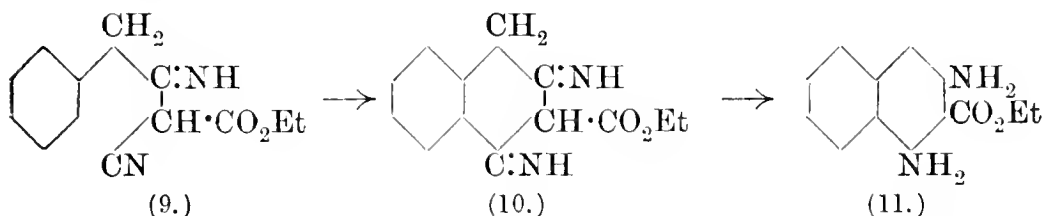


whereas a compound of formula (6), in which the nitrile group and the carboxyl group are united with the same carbon atom, cannot yield a derivative of glutazine under the same conditions.

The compound melting at 125° does not give phenylglutazine on treatment with concentrated sulphuric acid, and there can therefore be no doubt that it possesses a constitution represented by formula (6), a view which is confirmed by a close study of the compound which is actually formed with this reagent.

It has already been mentioned that one of our objects in investigating the interaction of benzyl cyanide and ethyl sodiocyanoacetate was to prepare a compound in which the nitrile group could by reason of its position pass into a six-membered carbon ring instead of the pyridine ring formed from the other compounds which have already been investigated.

This object will be more clearly understood when the formula of ethyl β -imino- α -cyano- γ -phenylbutyrate is written thus (9):

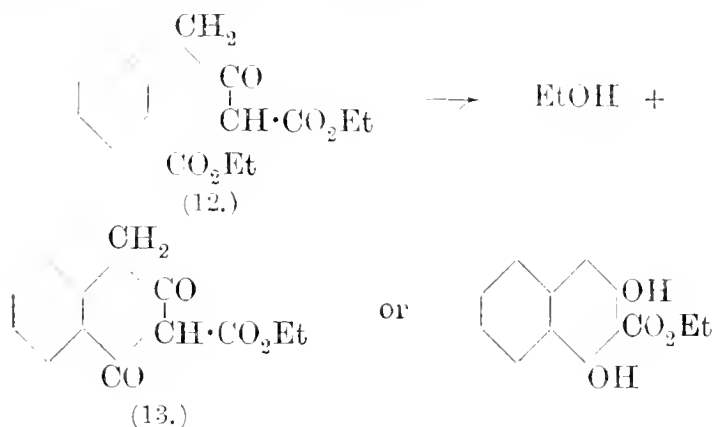


It was thought possible that the nitrile group might react with the ortho-hydrogen atom of the benzene ring, forming a di-imino-compound (10), which in its amino-form would be ethyl 1-3-diaminonaphthalene-2-carboxylate (11), and that by this means an interesting synthesis of the naphthalene ring might be effected.

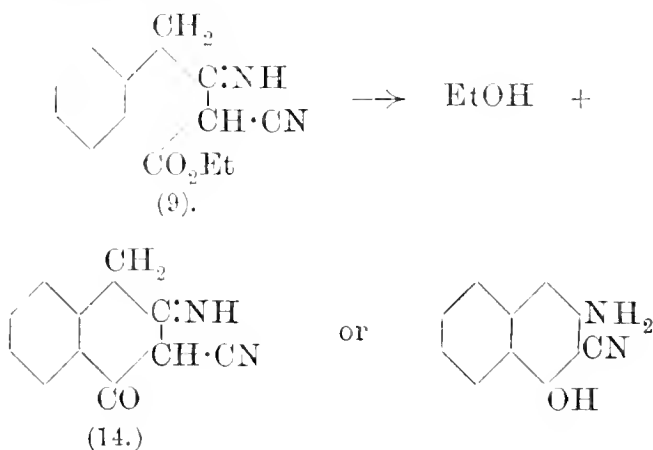
Since the original imino-compound (9) was formed in the presence of sodium ethoxide, we intended to attempt to obtain the di-imino-derivative (10) by treating ethyl β -imino- α -cyano- γ -phenylbutyrate with excess of this reagent. We were therefore considerably astonished to find that, on treating this ethyl salt with concentrated

sulphuric acid, in the attempt already mentioned to determine its constitution, it was quantitatively converted into the sulphate of ethyl 1:3-diaminonaphthalene-2-carboxylate (11).

This result was all the more surprising because it has been shown by Metzner (*Annalen*, 1901, 298, 386) that a similarly constituted compound, namely, ethyl phenylacetylmalonate (12), on treatment with cold, concentrated sulphuric acid, is converted with loss of alcohol into ethyl 1:3-dihydroxynaphthalene-2-carboxylate (13), the reaction taking place at the ordinary temperature,



and it was therefore to be expected that ethyl β -imino- α -cyano- γ -phenylbutyrate (9) would behave in the same way, yielding 3-amino-2-cyano-1-naphthol (14) :



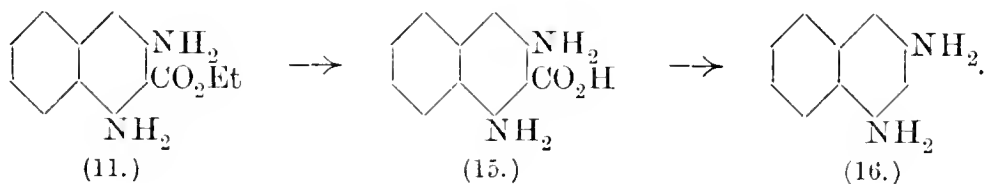
The yield, however, of ethyl 1:3-diaminonaphthalene-2-carboxylate (11) from ethyl β -imino- α -cyano- γ -phenylbutyrate (9), on treatment with sulphuric acid, is quantitative, and the reaction takes place with remarkable ease. Thus it is only necessary to add a quantity of well-ground ethyl salt to three times its weight of concentrated acid and allow the mixture to stand for one minute in order to complete the change. On first adding the ethyl salt it dissolves, forming a yellow solution which rapidly changes in colour in the course of a few seconds to deep malachite-green, heat at the same time being generated.

When this green solution is poured on ice the colour is discharged and a clear yellow solution is formed from which the sulphate of ethyl 1:3-diaminonaphthalene-2-carboxylate separates on standing as a pale yellow, crystalline precipitate. The sulphate is readily soluble in water, and if the aqueous solution is rendered alkaline the base is precipitated as an intense yellow crystalline compound, which, when purified by recrystallisation from alcohol, is obtained in deep yellow plates.

There can be no doubt that this yellow compound represents the di-imino-form of ethyl 1:3-diaminonaphthalene-2-carboxylate (10). The salts, especially the hydrochloride, can be obtained in almost colourless crystals, and they are therefore probably the salts of the amino-form (11). It is interesting to note, however, that although the solutions of these salts are colourless when cold, they become intensely coloured on boiling, the colour being again discharged on cooling.

The green colour which is formed when ethyl β -imino- α -cyano- γ -phenylbutyrate is treated with concentrated sulphuric acid is difficult to explain, since ethyl 1:3-diaminonaphthalene-2-carboxylate dissolves in the concentrated acid, forming a yellow solution which does not change on warming. That this coloration is not necessary for the production of the naphthalene ring is shown by the fact that if the solution of ethyl β -imino- α -cyano- γ -phenylbutyrate in concentrated sulphuric acid is brought about at 0°, and the temperature is not allowed to rise above this point, no green colour appears, the solution remaining a light brown. Whether the green colour is formed or not, the yield of the naphthalene is not apparently affected.

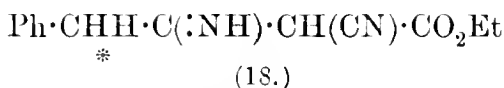
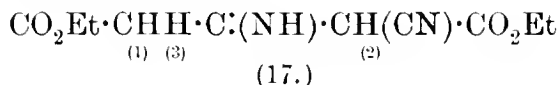
The corresponding carboxylic acid (15) can be readily prepared from ethyl 1:3-diaminonaphthalene-2-carboxylate (11) on treating it with an alcoholic solution of potash. The free acid, which is colourless, is unstable at temperatures above its melting point (85°), being then transformed with evolution of carbon dioxide into 1:3-naphthylenediamine (16).



1:3-Naphthylenediamine prepared in this way is identical with the compound obtained by Urban (*Ber.*, 1887, 20, 973) by the reduction of 1:3-dinitronaphthalene, and by Friedländer (*Ber.*, 1895, 28, 1953) by the action of ammonia on 4-amino-2-naphthol.

It was pointed out in Part I. of this series that ethyl β -imino- α -cyanoglutarate (17) reacted with sodium ethoxide, forming a sodium

derivative, and that the metal entered in the position (1), that after the sodium atom in this had been replaced by an alkyl radicle, the hydrogen marked (2) could be replaced by sodium, and that finally, after this sodium had been treated with an alkyl iodide, the third hydrogen atom marked (3) could be replaced.

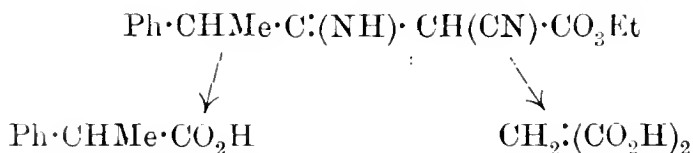


It is interesting to note that, although the hydrogen atom marked (2) is attached to the same carbon atom as a nitrile- and a carbethoxyl-group, yet the first hydrogen atom replaced is that marked (1), which is attached to the same carbon atom as the carbethoxyl- and the carbimino-group.

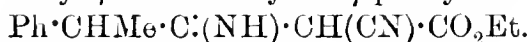
In the case of ethyl β -imino- α -cyano- γ -phenylbutyrate (18), the influence of the phenyl group is at once apparent, and we have only succeeded in introducing one alkyl group into this compound after repeatedly treating it with sodium ethoxide and the alkyl iodide. The hydrogen atom replaced is that marked (*), and apparently the hydrogen atom of the cyanoacetic residue is not replaceable under ordinary conditions.

We have carefully studied both the methyl and ethyl derivatives of ethyl β -imino- α -cyano- γ -phenylbutyrate, and have found that it is necessary to treat the ethyl salt four successive times with the calculated quantity of sodium ethoxide and excess of methyl (or ethyl) iodide in order to convert the whole of it into its mono-alkyl derivative.

The positions of the alkyl groups in the alkylated compounds can be readily shown by the products they give on complete hydrolysis with alcoholic potash. Thus the ethyl salt which is prepared by the action of sodium ethoxide and methyl iodide on ethyl β -imino- α -cyano- γ -phenylbutyrate gives phenylacetic and malonic acids under these conditions, thus:

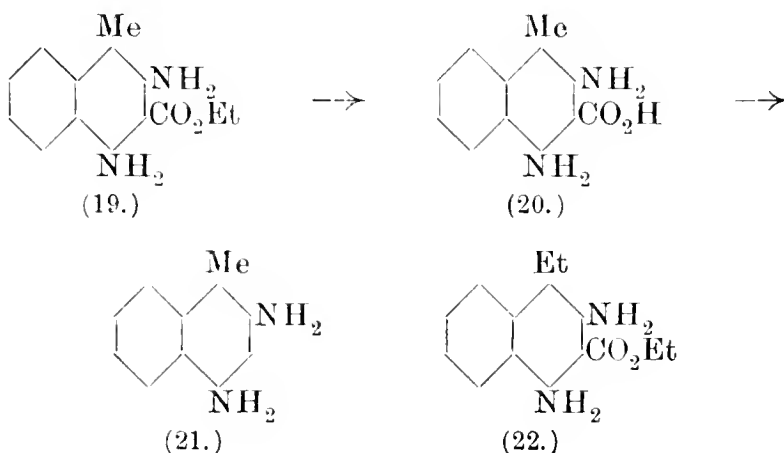


It is therefore ethyl β -imino- α -cyano- γ -phenyl-*n*-valerate,

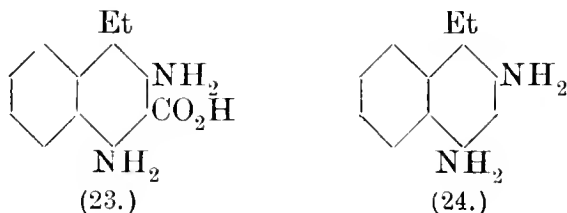


In the same way, the corresponding ethyl derivative gives a mixture of α -phenyl-*n*-butyric and malonic acids on complete alkaline hydrolysis. Its formula is therefore $\text{Ph} \cdot \text{CHEt} \cdot \text{C}(\text{NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$.

Both these ethyl salts behave in the same way as ethyl β -imino- α -cyano- γ phenylbutyrate on treatment with concentrated sulphuric acid. In each case a similar green to blue coloration is produced if the solution is allowed to become warm, but is not formed if the temperature is kept below 0° , and in each case, also, on pouring the mixture on ice a clear solution is obtained from which the sulphate of the base separates on standing. Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate (19) and ethyl 2:4-diamino-1-ethylnaphthalene-3-carboxylate (22) are in each case precipitated from the solutions of their sulphates on the addition of ammonia as yellow oils which on extraction by means of ether are obtained as syrups rapidly solidifying to yellow, crystalline solids.



Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate passes on hydrolysis with alcoholic potash into the corresponding carboxylic acid (20), which, like the unalkylated derivative, is a colourless, crystalline compound, decomposing with evolution of carbon dioxide on being heated above its melting point and passing into 2:4-diamino-1-methylnaphthalene (21).



In the same way, ethyl 2:4-diamino-1-ethylnaphthalene-3-carboxylate (22) yields 2:4-diamino-1-ethylnaphthalene-3-carboxylic acid (23) and 2:4-diamino-1-ethylnaphthalene (24).

The Condensation of Benzyl Cyanide with its Sodium Derivative.

The interaction of benzyl cyanide with its sodium derivative was first studied by Wache (*J. pr. Chem.*, 1889, ii, **39**, 251), who investi-

gated the action of finely divided sodium on an ethereal solution of the nitrile. Although this chemist was unable to isolate the bimolecular nitrile, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, he found that, on heating the precipitate formed in the above reaction with excess of benzyl cyanide in a sealed tube at 180° for several hours, it was transformed into a white, crystalline, basic substance of the empirical formula $\text{C}_{24}\text{H}_{21}\text{N}_3$, to which he gave the name of cyanbenzylidine (6-amino-5-phenyl-2:4-dibenzylpyrimidine), and the formula $\text{CH}_2\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{C}(\text{CH}_2\text{Ph}) \\ \text{N}-\text{C}(\text{NH}_2) \end{smallmatrix}\text{CPh}$, on account of the similarity between its mode of formation and properties and those of cyanethine and cyanmethine, which E. v. Meyer (*J. pr. Chem.*, 1889, ii, 39, 156) had previously shown to be derivatives of pyrimidine. Wache subsequently found that the best way to prepare cyanbenzylidine was to heat a mixture of the nitrile and dry sodium ethoxide in a sealed tube at $170\text{--}180^\circ$ for many hours.

E. v. Meyer (*J. pr. Chem.*, 1895, ii, 52, 114), in conjunction with O. Probst (*Inaug. Diss. Leipzig*, 1894), repeated the work of Wache, and found that if the precipitate which was formed by the action of finely divided sodium on an ethereal solution of benzyl cyanide was washed with light petroleum and then added to dilute acetic acid, a viscid oil was obtained which could not be distilled without undergoing decomposition, but which evidently consisted of β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, since on treatment with hydroxylamine it gave the same oxime as that derived from cyanodibenzyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$. Later, v. Walther and Schickler (*J. pr. Chem.*, 1897, ii, 55, 350) prepared the same compound by the action of ammonia on the cyanoketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$, but also failed to obtain it in the solid condition.

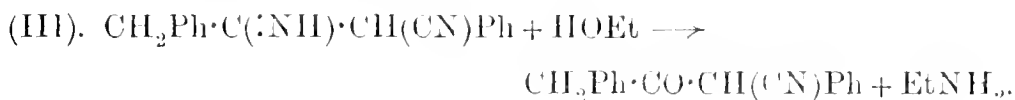
The termolecular nitrile cyanbenzylidine was thoroughly investigated by Herfeldt (*J. pr. Chem.*, 1896, ii, 53, 246), who prepared many of its derivatives, and still more recently v. Walther (*J. pr. Chem.*, 1903, ii, 67, 447) has found that it can be prepared by the action of finely divided sodium on an ethereal solution of benzyl cyanide containing dimethylaniline. Owing to the similarity in constitution between benzyl cyanide and ethyl cyanoacetate, we decided, in order to prepare β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, to investigate the interaction of benzyl cyanide with its sodium derivative in alcoholic solution, since in the case of ethyl cyanoacetate a good yield of ethyl β -iminocyanoglutarate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{CO}_2\text{Et}$, had been obtained by Baron, Remfry, and Thorpe by this means (*Trans.*, 1904, 85, 1726).

We found that the products formed in this condensation varied with the length of time during which the heating was continued at 100° . Thus, when two molecular equivalents of benzyl cyanide and one of

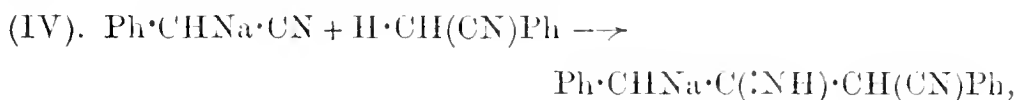
sodium ethoxide dissolved in alcohol were heated on the water-bath for half an hour, the product consisted of about 70 per cent. of β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, mixed with unchanged benzyl cyanide. When the heating was prolonged, an odour resembling ammonia became apparent at the mouth of the condenser and on working up the product at the end of two hours it was found to consist of about equal proportions of β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{:NH})\cdot\text{CH}(\text{CN})\text{Ph}$, β -keto- α -cyano- $\alpha\gamma$ -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$, and cyanbenzylidine, some benzyl cyanide being at the same time recovered unchanged.

On prolonging the heating until the odour resembling ammonia ceased to be perceptible, an operation which usually required twenty-four hours to accomplish, the product was found to consist entirely of β -keto- α -cyano- $\alpha\gamma$ -diphenylpropane and cyanbenzylidine.

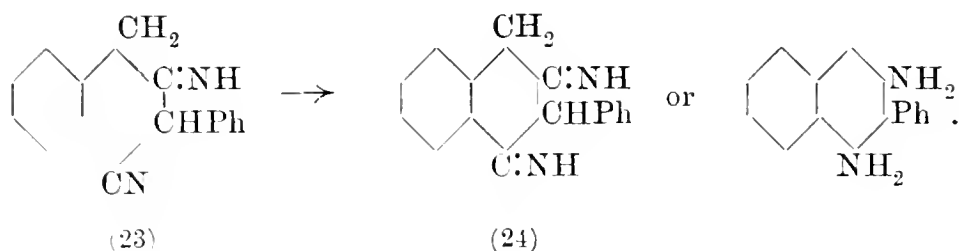
Subsequently it was found by experiment that the odour resembling ammonia was not due to this substance itself, but to ethylamine, which was probably formed by the action of the alkaline alcoholic solution on β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane, the reaction evidently proceeding according to equation (III):



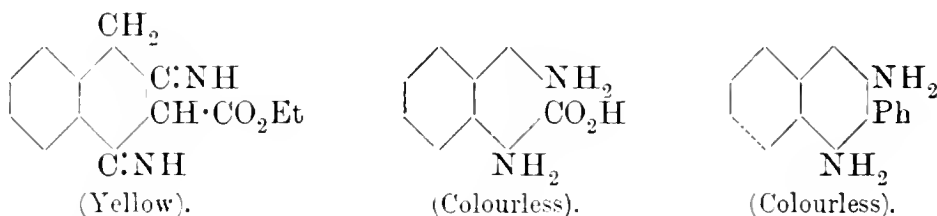
It is apparent, therefore, that the first action of benzyl cyanide on its sodium derivative in alcoholic solution at 100° is to form β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane according to equation (IV):



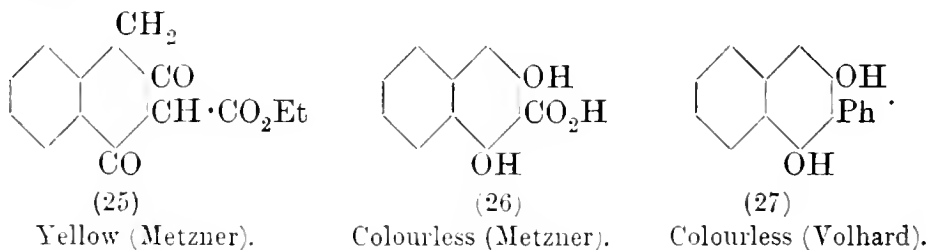
and that if the reaction is stopped at the end of about half an hour a good yield of this compound can be obtained. After this time, the initial product is slowly decomposed in accordance with equation (III) and β -keto- α -cyano- $\alpha\gamma$ -diphenylpropane is formed; at the same time, the sodium derivative of β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane reacts with the unchanged benzyl cyanide, forming cyanbenzylidine in accordance with the observation of Wache. Like all previous investigators, we have been unable to obtain β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane (23) in a crystalline condition, although we find that it can be distilled without decomposition under a pressure of 20 mm. if the operation is conducted rapidly and only small quantities are used. When treated with cold concentrated sulphuric acid, it behaves in just the same way as ethyl β -imino- α -cyano- γ -phenylbutyrate, being converted into 1:3-diamino-2-phenylnaphthalene (24) thus:



It is worthy of note that, whereas ethyl 1:3-diaminonaphthalene-2-carboxylate is intense yellow in colour, 1:3-diamino-2-phenylnaphthalene is colourless, and a comparison of the three following formulæ is of interest as showing the influence of the carbethoxyl, carboxyl, and phenyl groups respectively on the stable forms of similar compounds:



It is also of interest to note that the same phenomenon occurs in the corresponding hydroxy-compounds, thus: Metzner (*Annalen*, 1901, 298, 386) finds that ethyl 1:3-dihydroxynaphthalene-2-carboxylate (25) is yellow, whereas the corresponding acid (26) is colourless. 1:3-Dihydroxy-2-phenylnaphthalene (27), which has been prepared by Volhard (*Annalen*, 1900, 296, 16) by the action of concentrated sulphuric acid on ethyl diphenylacetoacetate, $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{CH}(\text{Ph}) \cdot \text{CO}_2\text{Et}$, is also colourless.



The salts of 1:3-diamino-2-phenylnaphthalene are colourless, but become intensely coloured on exposure to the air. A full investigation of its properties are in progress.

EXPERIMENTAL.

Formation of Ethyl β-Imino-α-cyano-γ-phenylbutyrate, $\text{CH}_2\text{Ph} \cdot \text{C}(\text{:NH}) \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}.$

This ester was produced by the condensation of the sodium derivative of ethyl cyanoacetate with benzyl cyanide in alcoholic solution. Twenty-three grams of sodium were dissolved in 275 grams of alcohol and mixed with 113 grams of ethyl cyanoacetate. To

the well-cooled solution 117 grams of benzyl cyanide were added and the whole heated on the water-bath. It was found that the yield of the condensation product varied considerably with the length of time during which the mixture was heated and that much care had to be exercised in order to obtain the above compound in yields sufficiently large for the purposes of the research. This was necessary owing to the fact that soon after being formed, the condensation product was found to pass rapidly into another compound (see below) which has not yet been identified. This difficulty will be realised when it is pointed out that after the above mixture had been heated for twelve hours at 100° only about 10 per cent. of ethyl β -imino- α -cyano- γ -phenylbutyrate could be isolated, the majority of the benzyl cyanide being recovered unchanged, whereas if the heating was prolonged at the same temperature for twenty-four hours the product, whilst containing 25 per cent. of the ester, was found to be mixed with as much as 40—45 per cent. of another compound of high molecular weight, and only a relatively small proportion of the benzyl cyanide was recovered unchanged. On heating for a still longer time the quantity of the complex substance increased and the amount of ethyl β -imino- α -cyano- γ -phenylbutyrate formed and of unchanged benzyl cyanide diminished.

After numerous experiments carried out under different conditions in which yields of the ethyl ester varying from 10—50 per cent. of the theoretical amount were obtained, the following method was ultimately adopted as being the most convenient.

The molecular mixture described above was heated on the steam-bath for fifteen hours, the flask being vigorously shaken from time to time. It was observed that the white insoluble sodium derivative of ethyl cyanoacetate gradually dissolved and that the solution became deep red in colour and very viscous. After being heated for the specified time the product was cooled, when it set to a thick jelly. Dilute hydrochloric acid was then added and the heavy oil which separated extracted by means of ether, the ether solution being washed with water and then with dilute sodium carbonate solution. During the washing with sodium carbonate a considerable quantity of acid oil was extracted, a description of which will be found below.

The ether solution, without being dried, was evaporated free from ether, and the residue subjected to distillation in a current of steam, whereby the whole of the unchanged benzyl cyanide was recovered in the distillate. The residue, which consisted of a viscid brown oil solidifying on cooling, was then separated by filtration, dried on a porous plate, and recrystallised from absolute alcohol.

Ethyl β -imino- α -cyano- γ -phenylbutyrate, purified in this way, was obtained in long, colourless needles, which melted at 125° :

0.1877 gave 0.4659 CO_2 and 0.1068 H_2O . $\text{C} = 67.69$; $\text{H} = 6.32$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 67.81$; $\text{H} = 6.1$ per cent.

The ethyl ester is insoluble in solutions of alkali carbonates and in aqueous caustic alkalis and is not acted on, even on prolonged boiling, by concentrated hydrochloric acid. It can be recrystallised from either methyl or ethyl alcohol or from benzene, but is almost insoluble in light petroleum.

The sodium carbonate washings from the ether solution were acidified, when a heavy oil separated, which partially solidified. This was filtered by the aid of the pump and the mixture of oil and solid washed with ether, in which solvent the solid was found to be quite insoluble. The residue was dried on a porous plate and found to consist of a light brown amorphous substance apparently insoluble in all the usual organic solvents with the exception of hot glacial acetic acid in which it was only very sparingly soluble. It was insoluble in concentrated hydrochloric acid, but dissolved in concentrated sulphuric acid apparently unchanged, since it was reprecipitated on the addition of water. It is, however, readily soluble in dilute solutions of alkali carbonates and in caustic alkalis and in the latter case on the addition of excess of the alkali a crystalline alkali salt slowly separates. This salt is, however, difficult to purify since it is dissociated by water, and therefore cannot be freed from the excess of alkali. For the purpose of analysis the compound was purified by conversion into the potassium salt, which was effected by first washing the crude product thoroughly with ether and then dissolving it in a moderately dilute solution of caustic potash. On standing a crystalline *potassium* salt slowly separated which was filtered and reconverted into the original acid by treatment with dilute hydrochloric acid. The white amorphous precipitate thus obtained was then recrystallised from a large quantity of glacial acetic acid, from which solvent it separated in colourless, microscopic needles which melted to a brown liquid at 335° ; *

I. 0.3086 gave 0.8346 CO_2 and 0.1416 H_2O . $\text{C} = 73.76$; $\text{H} = 5.14$.

II. 0.2072 „ 0.5610 CO_2 „ 0.0940 H_2O . $\text{C} = 73.84$; $\text{H} = 5.08$.

III. 0.2508 „ 35.0 c.c. nitrogen at 18° and 767 mm. $\text{N} = 15.95$.

$\text{C}_{21}\text{H}_{18}\text{ON}_4$ requires $\text{C} = 73.7$; $\text{H} = 5.2$; $\text{N} = 16.4$ per cent.

These figures furnish no clue as to the identity of the substance.

Considerable quantities of this compound having accumulated during the course of this research, it is our intention further to investigate its properties.

The ethereal layer which floated on the filtrate from the above

* This melting point was taken in cyanbenzylidene (see p. 1932).

compound after washing it free from oil was separated in the funnel, washed with water, dried and the ether evaporated. The residue, which consisted of a viscid, dark oil readily soluble in dilute sodium carbonate solution, was, without further purification, mixed with three times its volume of absolute alcohol and an equal volume of concentrated sulphuric acid and after being allowed to stand for twelve hours, heated on the water-bath for three hours. The mixture was then poured into water, the oil which separated extracted with ether, and after any unchanged acid had been extracted by means of dilute sodium carbonate solution, the ethereal solution was dried and evaporated free from ether. The brown liquid which remained deposited a considerable quantity of crystals on standing, and these were collected and purified by recrystallisation from hot alcohol, being obtained in silky needles melting at 178° :

- I. 0.1868 gave 0.5252 CO_2 and 0.0882 H_2O . C = 76.68 ; H = 5.28.
 II. 0.1950 „ 0.5472 CO_2 „ 0.0908 H_2O . C = 76.52 ; H = 5.17.
 III. 0.2284 „ 24.6 c.c. nitrogen at 13° and 756 mm. N = 12.78.
 IV. 0.2264 „ 24.6 c.c. „ „ 13° „ 752 mm. N = 12.81.
 $\text{C}_{21}\text{H}_{17}\text{ON}_3$ requires C = 77.0 ; H = 5.2 ; N = 12.9 per cent.

The compound is insoluble in alkalis and in concentrated hydrochloric acid. Its constitution has not yet been determined.

The Constitution of Ethyl β -Imino- α -cyano- γ -phenylbutyrate.

Formation of Phenylacetic and Malonic Acids by the Action of Methyl Alcoholic Potash.

The proof of the constitution of ethyl β -imino- α -cyano- γ -phenylbutyrate was derived from a study of the products which were formed when it was completely hydrolysed by means of an alcoholic solution of potash. As already mentioned in the introduction, this proof is not in itself conclusive, since ethyl β -imino- γ -cyano- γ -phenylbutyrate, $\text{CHPh}(\text{CN})\cdot\text{C}(\text{:NH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which might conceivably be formed in the same reaction would also give the same products on alkaline hydrolysis, but that, taken in conjunction with the other reactions of this ethyl salt, places its constitution beyond question.

When ethyl β -imino- α -cyano- γ -phenylbutyrate was mixed with a solution of $1\frac{1}{2}$ times the calculated quantity of potash dissolved in methyl alcohol, considerable heat was generated and much ammonia was evolved on heating the solution on the water-bath. After heating for six hours the evolution of ammonia had ceased and a clear solution was obtained on pouring the hydrolysed product into water. The excess of methyl alcohol was then evaporated and the residue acidified by means of hydrochloric acid, when a white, crystalline substance

separated. This was collected and recrystallised from dilute alcohol, being thus obtained in glistening plates melting at 76° . An analysis proved, as its appearance and odour indicated, that it was phenylacetic acid:

0.2107 gave 0.5222 CO_2 and 0.1232 H_2O . $\text{C} = 67.61$; $\text{H} = 6.49$.

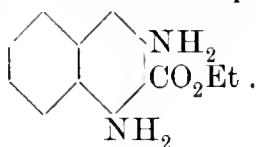
$\text{C}_7\text{H}_8\text{O}_2$ requires $\text{C} = 67.8$; $\text{H} = 6.4$ per cent.

The filtrate from the phenylacetic acid was evaporated to dryness, acidified with concentrated hydrochloric acid and again evaporated, being finally placed in a Soxhlet apparatus and extracted with ether. The ethereal solution on drying and evaporating deposited a quantity of oil which rapidly solidified and then melted at 132° with decomposition. The analysis, together with the fact that on distillation it yielded acetic acid, showed it to be malonic acid:

0.2217 gave 0.2796 CO_2 and 0.0778 H_2O . $\text{C} = 34.39$; $\text{H} = 3.89$.

$\text{C}_3\text{H}_4\text{O}_4$ requires $\text{C} = 34.6$; $\text{H} = 3.8$ per cent.

Formation of Ethyl 1:3-Diaminonaphthalene-2-carboxylate,



When dry ethyl β -imino- α -cyano- γ -phenylbutyrate ground to a fine powder is added to three times its weight of cold, concentrated sulphuric acid it dissolves rapidly forming a yellow solution. If the mixture is allowed to become warm this solution becomes deep malachite-green in colour, but it remains yellow if placed in a mixture of ice and salt. If, as soon as the ethyl salt has all dissolved, an operation which usually takes about one minute, the strong sulphuric acid solution is poured on ice, a clear yellow solution is produced from which an almost white crystalline substance separates on standing. This compound is the *sulphate*, $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$, of the above base and can be obtained in almost colourless plates by recrystallisation from water:

0.1539 gave 0.2706 CO_2 and 0.0705 H_2O . $\text{C} = 47.95$; $\text{H} = 5.12$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 47.6$; $\text{H} = 4.9$.

The sulphate gradually becomes yellow on exposure to the air, and when dissolved in water forms, in the cold, an almost colourless solution, which on warming becomes bright yellow; this yellow colour is discharged on cooling.

Ethyl-1:3-diaminonaphthalene-2-carboxylate is precipitated as a yellow, crystalline solid on adding aqueous ammonia to a solution of the sulphate dissolved in water. It was collected by filtration and

recrystallised from ether, being obtained in this way in golden yellow plates melting at 108° :

0.2244 gave 0.5568 CO_2 and 0.1262 H_2O . $\text{C} = 67.65$; $\text{H} = 6.24$.

0.3238 „ 32.4 c.c. of nitrogen at 12° and 769 mm. $\text{N} = 12.13$.

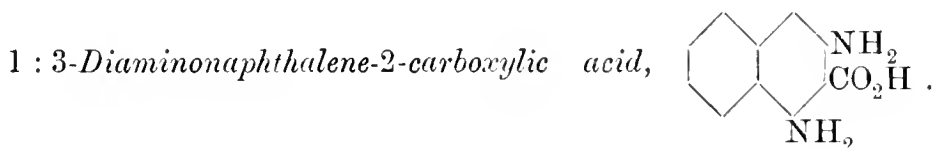
$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 67.8$; $\text{H} = 6.1$; $\text{N} = 12.2$ per cent.

The *hydrochloride*, $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$, is best prepared by dissolving the base in dilute hydrochloric acid and then adding excess of concentrated hydrochloric acid to the almost colourless solution. On standing, colourless needles of the above salt separate :

0.2911 gave 0.2734 AgCl . $\text{Cl} = 23.30$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 23.4$ per cent.

Ethyl 1 : 3-diaminonaphthalene-2-carboxylate is very readily oxidised by the mildest oxidising agents, being even slowly altered on exposure to the air. The compounds produced in these circumstances as well as the products formed by the action of nitrous acid on this ethyl salt are still under investigation,



This acid was prepared from the ethyl salt by hydrolysing it with methyl alcoholic potash. 5 grams were added to a solution of $1\frac{1}{2}$ times the calculated quantity of caustic potash dissolved in methyl alcohol and the solution warmed on the water-bath. On cooling a crystalline *potassium* salt, $\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{K}$, separated, which was collected by filtration, purified by washing with a little methyl alcohol, and dried on a porous plate. It is a yellow, crystalline solid readily soluble in water :

0.2195 gave 0.0788 K_2SO_4 . $\text{K} = 16.09$.

$\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{K}$ requires $\text{K} = 16.25$ per cent.

The free acid is precipitated as a white, crystalline solid on adding dilute hydrochloric acid to a solution of the potassium salt in water. It was collected by filtration, dried on a porous plate and recrystallised from warm water. Since the acid rapidly loses carbon dioxide at 80° , it is necessary that the aqueous solution should be considerably below this temperature. Since, however, the acid is readily soluble in warm water and separates again on cooling, it can easily be recrystallised in quantities without raising the temperature of the solution above 60° . 1 : 3-Diaminonaphthalene-2-carboxylic acid can be obtained in this

way in colourless needles melting at 85° with immediate elimination of carbon dioxide:

0.2258 gave 0.5374 CO_2 and 0.1064 H_2O . $\text{C} = 64.90$; $\text{H} = 5.27$.

$\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C} = 65.3$; $\text{H} = 4.9$ per cent.

The carboxylic acid does not form salts with acids.

1 : 3-Naphthylenediamine.

This base was prepared from the above carboxylic acid by heating it at 100° until the evolution of carbon dioxide had ceased. The operation was carried out in a small flask which was placed in a bath of sulphuric acid and heated to the requisite temperature. When the evolution of gas had ceased, the product was dissolved in dilute hydrochloric acid and the deep red solution, after filtering, rendered alkaline with caustic potash. The base, which was then precipitated, was recrystallised from water and obtained in small plates, usually slightly red in colour, which melted at 96° :

0.1622 gave 0.4520 CO_2 and 0.0910 H_2O . $\text{C} = 76.00$; $\text{H} = 6.28$.

$\text{C}_{10}\text{H}_{10}\text{N}_2$ requires $\text{C} = 76.0$; $\text{H} = 6.3$ per cent.

The diacetyl derivative, $\text{C}_{10}\text{H}_8\text{N}_2(\text{CO}\cdot\text{CH}_3)_2$ was prepared by dissolving the base in acetic anhydride and heating the solution on the sand-bath for one hour. The excess of the anhydride was then evaporated by placing the solution in an evacuated desiccator over potash until solid. Recrystallised from acetic acid, it was obtained in fine needles melting at $263\text{--}265^{\circ}$ (Friedlander, *Ber.*, 1895, 28, 1953):

0.1693 gave 0.3826 CO_2 and 0.1112 H_2O . $\text{C} = 61.64$; $\text{H} = 7.29$.

$\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 61.9$; $\text{H} = 7.2$ per cent.

Formation of Ethyl β -Imino- α -cyano- γ -phenylvalerate,



As stated in the introduction, the methylation of ethyl β -imino- α -cyano- γ -phenylbutyrate by means of sodium ethoxide and methyl iodide in alcoholic solution is not easily accomplished. The difficulty is probably due to the fact that the unreactive character of the methylene hydrogen atom causes a state of equilibrium to be set up between the sodium ethoxide, the ethyl salt and its sodium derivative, in which only about one-third of the last-named is formed. Thus, by the action of methyl iodide on a cold mixture of equimolecular proportions of sodium ethoxide and ethyl β -imino- α -cyano- γ -phenylbutyrate, only about one-third of the ethyl salt is converted into its methyl derivative. Therefore, in order to complete the conversion,

the process of methylation was repeated four times in the following manner :

Ten grams of the ethyl salt were added to a solution containing 1 gram of sodium dissolved in 12 grams of alcohol, and the whole, after being well cooled, treated with 12 grams of methyl iodide. After standing for some time in the cold the mixture was heated on the water-bath until a test portion diluted with water gave a neutral reaction with litmus, when, after the excess of alcohol and unchanged methyl iodide had been distilled off as completely as possible on the water-bath, a further quantity of sodium ethoxide made by dissolving 1 gram of sodium in 12 grams of alcohol was added, and the solution treated with methyl iodide and again heated until neutral. After this process had been repeated four times, water was added and the oil, which then separated and which almost immediately solidified, was filtered by the aid of the pump and purified by recrystallisation from alcohol. *Ethyl β -imino- α -cyano- γ -phenylvalerate* is obtained in this way in large needles melting at 92° :

0.1596 gave 0.4052 CO_2 and 0.0959 H_2O . C = 69.24 ; H = 6.72.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ requires C = 68.8 ; H = 6.6 per cent.

Formation of α -Phenylpropionic Acid and Malonic Acid from Ethyl β -Imino- α -cyano- γ -phenylvalerate.

The proof of the constitution of ethyl β -imino- α -cyano- γ -phenyl- γ -methylbutyrate was derived from the study of the products formed from it on alkaline hydrolysis. The operation was carried out as follows :

Five grams of the ethyl salt were mixed with a solution containing one-and-a-half times the calculated quantity of caustic potash dissolved in methyl alcohol and heated on the water-bath until the odour of ammonia, which was apparent at the commencement of the hydrolysis, had entirely disappeared. The product was then diluted with water and evaporated on the water-bath until free from methyl alcohol, when it was acidified with concentrated hydrochloric acid and allowed to stand. Since the oil which separated on the addition of the acid showed no tendency to crystallise, the solution was extracted by means of ether and the ethereal solution, after drying, evaporated free from ether. The oil which remained was then distilled under the ordinary pressure and was found to boil constantly at 264 — 265° , at which temperature α -phenylpropionic acid, which does not appear to be a solid at the ordinary temperature, boils (Fittig and Wurster, *Annalen*, 1879, **195**, 165) :

0.2100 gave 0.5532 CO_2 and 0.1295 H_2O . C = 71.84 ; H = 6.85.

$\text{C}_9\text{H}_{10}\text{O}_2$ requires C = 72.0 ; H = 6.7 per cent.

The aqueous solution after the extraction of the above acid was evaporated to dryness and extracted in a Soxhlet apparatus with ether. The ethereal solution after drying was evaporated free from ether yielding a solid residue which melted at 132° and gave acetic acid on distillation, evidently therefore consisting of malonic acid:

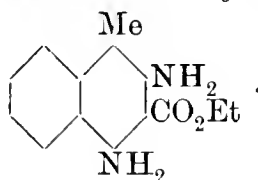
0.1774 gave 0.2237 CO_2 and 0.0622 H_2O . $\text{C} = 34.41$; $\text{H} = 3.90$.

$\text{C}_3\text{H}_4\text{O}_4$ requires $\text{C} = 34.6$; $\text{H} = 3.8$ per cent.

The above analysis indicates that the substance is malonic acid and not methylmalonic acid, and therefore shows that only one methyl group had entered into the molecule of ethyl β -imino- α -cyano- γ -phenylbutyrate on its being completely methylated in the manner already described.

Owing to there being only a slight difference between the percentage compositions of ethyl β -imino- α -cyano- γ -phenylbutyrate and its methyl derivative, this fact could not be definitely settled on the results of their analysis alone.

Formation of Ethyl 2:4-Diamino-1-methylnaphthalene-3-carboxylate,



The conversion of ethyl β -imino- α -cyano- γ -phenylvalerate into the above derivative of naphthalene takes place with the same ease as that already described in the case of the unmethylated derivative. Five grams of the finely-ground ethyl salt were added slowly to three times its weight of concentrated sulphuric acid cooled in ice. On each addition, the salt instantly dissolved, and in spite of the low temperature the sulphuric acid solution became deep bluish-green. When all had been added, the solution was allowed to stand for two or three minutes and then poured on ice. The deep bluish-green colour of the solution was instantly discharged on mixing with the ice, forming a clear yellow solution from which the *sulphate*, $\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$, of the base slowly separated on standing as a pale yellow, crystalline precipitate:

0.1708 gave 0.3064 CO_2 and 0.0828 H_2O . $\text{C} = 48.92$; $\text{H} = 5.42$.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 49.1$; $\text{H} = 5.3$ per cent.

The sulphate is readily soluble in hot water, but separates from its concentrated solutions in this solvent on cooling. An aqueous solution of the salt at 0° is nearly colourless, but becomes a deep yellow on being heated to the boiling point. On being again cooled, the colour

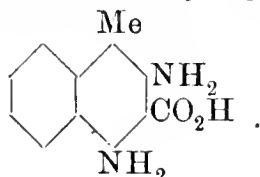
is discharged. The sulphate is insoluble in alcohol and this fact can be utilised in its formation, since on pouring the bluish-green sulphuric acid solution into three times its volume of well-cooled absolute alcohol, the salt is completely precipitated and can be isolated by filtration. The free base was prepared by dissolving the sulphate in water and adding ammonia until strongly alkaline. The deep yellow oil which was then precipitated did not show any signs of crystallising, and was therefore extracted by means of ether, the ethereal solution being washed with a little water, dried with calcium chloride, and evaporated. The yellow syrup which remained instantly solidified on scratching, forming a deep yellow solid, which was recrystallised from methyl alcohol and thus obtained in orange-yellow prisms melting at 75° :

0.1676 gave 0.4245 CO_2 and 0.1017 H_2O . $\text{C} = 69.08$; $\text{H} = 6.74$.

$\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C} = 68.8$; $\text{H} = 6.6$ per cent.

Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate is readily soluble in cold ether and can in this way be distinguished from the lower homologue. It is also soluble in all the usual organic solvents excepting light petroleum, and is readily oxidised, but is not altered on exposure to the air so rapidly as ethyl 1:3-diaminonaphthalene-2-carboxylate.

Formation of 2:4-Diamino-1-methylnaphthalene-3-carboxylic Acid,

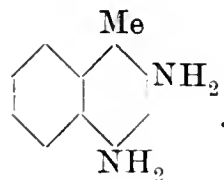


This acid was prepared from the ethyl salt by the action of alcoholic potash. Ethyl 2:4-diamino-1-methylnaphthalene-3-carboxylate was added to a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol and the mixture heated on the water-bath until a test portion diluted with water remained clear. Water was then added and the solution evaporated on the water-bath until free from methyl alcohol, when it was acidified, and the colourless, glistening leaflets of the acid which then separated collected by filtration. The acid, which is slowly decomposed by boiling water, was recrystallised rapidly from hot water, and obtained in this way in colourless needles which decomposed with evolution of carbon dioxide at $155-160^{\circ}$ apparently without melting:

0.1697 gave 0.4139 CO_2 and 0.0875 H_2O . $\text{C} = 66.52$; $\text{H} = 5.73$.

$\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 66.7$; $\text{H} = 5.6$ per cent.

Formation of 2:4-Diamino-1-methylnaphthalene,



This base was prepared from the carboxylic acid by heating it for some time at 180° . The finely-ground and purified acid was placed in a small flask and heated in a bath of sulphuric acid at the required temperature until carbonic acid ceased to be evolved, when the residue was treated with dilute hydrochloric acid, and the deep red solution thus formed boiled with animal charcoal and filtered. On adding dilute aqueous caustic soda to the filtrate, the base was precipitated as a resin, which did not crystallise on standing. It was therefore dissolved in concentrated hydrochloric acid and the solution allowed to stand, when the *hydrochloride*, $C_{11}H_{12}N_2 \cdot 2HCl$, slowly separated in white, silky needles:

0.2117 gave 0.2467 AgCl. Cl = 28.91.

$C_{11}H_{12}N_2 \cdot 2HCl$ requires Cl = 29.0 per cent.

The hydrochloride readily dissolved in water, and the solution on being made alkaline with caustic soda solution deposited the base as a white solid, which, when recrystallised from dilute methyl alcohol, was obtained in fine, white needles melting at 65° :

0.1912 gave 0.5358 CO_2 and 0.1245 H_2O . C = 76.43; H = 7.23.

$C_{11}H_{12}N_2$ requires C = 76.7; H = 7.0 per cent.

The base becomes slowly coloured on exposure to air and light.

The *platinichloride*, $C_{11}H_{12}N_2 \cdot H_2PtCl_6$, is precipitated as a yellow, crystalline powder on adding excess of platinic chloride to a solution of the hydrochloride of the base in water:

0.2513 gave 0.0839 Pt. Pt = 33.38.

$C_{11}H_{12}N_2 \cdot H_2PtCl_6$ requires Pt = 33.5 per cent.

Formation of Ethyl β -Imino- α -cyano- γ -phenyl-n-benzoate,
 $Ph \cdot CHEt \cdot C(:NH) \cdot CH(CN) \cdot CO_2Et$.

The preparation of the ethyl derivative of ethyl β -imino- α -cyano- γ -phenylbutyrate was undertaken in order to show conclusively that only one alkyl group could be introduced into this compound by the action of sodium ethoxide and an alkyl iodide. The process adopted was the same as that already described in the case of the methyl derivative, only in the present instance even greater difficulty was experienced in introducing the alkyl group, and, after the process of ethylation

had been repeated four times, considerable quantities of unchanged ethyl salt were recovered. The actual operation was carried out as follows: 10 grams of ethyl β -imino- α -cyano- γ -phenylbutyrate were added to a solution containing 2 grams of sodium in 30 grams of alcohol, which, after being well cooled, was mixed with 24 grams of ethyl iodide and warmed on the water-bath until a test portion diluted with water showed a neutral reaction to litmus. The excess of alcohol and ethyl iodide was then distilled off as far as possible on the water-bath and the above process again repeated. When the treatment had been carried out four times, water was added, and the oil, which was then precipitated and which solidified on standing, separated by filtration. In the first place, the solid was recrystallised from dilute methyl alcohol, from which solvent it separated in needles having a melting point of $60-80^\circ$. These were then ground with cold benzene, in which a considerable quantity dissolved, leaving a residue which melted at $124-125^\circ$.

The following analysis showed this substance to be unchanged ethyl β -imino- α -cyano- γ -phenylbutyrate:

0.1554 gave 0.3888 CO_2 and 0.0903 H_2O . $\text{C} = 68.23$; $\text{H} = 6.50$.

$\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C} = 67.8$; $\text{H} = 6.1$ per cent.

The benzene filtrate on evaporation left a residue which melted at $60-65^\circ$, which was again ground with cold benzene yielding a further small quantity of unchanged ethyl β -imino- α -cyano- γ -phenylbutyrate.

The benzene solution from this second separation gave a product which melted at $60-61^\circ$. This was finally recrystallised from methyl alcohol, pure ethyl β -imino- α -cyano- γ -phenyl-n-hexoate being thus obtained in small prisms melting at 60° :

0.1564 gave 0.3990 CO_2 and 0.0996 H_2O . $\text{C} = 69.58$; $\text{H} = 7.12$.

$\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 69.8$; $\text{H} = 7.0$ per cent.

Formation of α -Phenylbutyric Acid, $\text{Ph}\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{H}$, and Malonic Acid from Ethyl β -Imino- α -cyano- γ -phenyl-n-hexoate.

The position of the ethyl group in ethyl β -imino- α -cyano- γ -phenyl-ethylbutyrate was determined by the products formed on its complete hydrolysis with methyl alcoholic potash. Five grams of the ethyl salt were heated on the water-bath with a solution containing one-and-a-half times the calculated quantity of caustic potash dissolved in methyl alcohol until the odour of ammonia has ceased to be apparent. Water was then added and the solution evaporated on the water-bath until free from methyl alcohol, when it was acidified with hydrochloric acid and the product allowed to stand. The oil which was first pre-

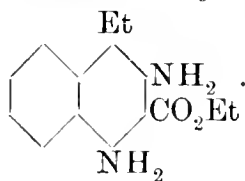
precipitated on the addition of the acid became solid on standing and was isolated by filtration. Recrystallised from dilute alcohol it was obtained in crystals melting at 42° which is the correct melting point of α -phenylbutyric acid (Neure, *Annalen*, 1889, 250, 154) :

0.2001 gave 0.5358 CO_2 and 0.1333 H_2O . $\text{C} = 73.03$; $\text{H} = 7.40$.

$\text{C}_{10}\text{H}_{12}\text{O}_2$ requires $\text{C} = 73.2$; $\text{H} = 7.3$ per cent.

The aqueous filtrate after extraction with ether was evaporated to dryness on the water-bath, and the residue extracted in a Soxhlet apparatus with ether. The ether solution, after being dried with calcium chloride, was evaporated free from ether, yielding a white solid melting at 132° , which was converted on distillation into acetic acid. It was evidently, therefore, malonic acid, and its formation together with that of α -phenylbutyric acid indicates clearly that the ethyl group in ethyl β -imino α -cyano- γ -phenyl- γ -ethylbutyrate is attached to the same carbon atom as is the benzene nucleus.

Formation of Ethyl 2:4-Diamino-1-ethylnaphthalene-3-carboxylate,



The conversion of ethyl β -imino α -cyano- γ -phenyl- n -hexoate into the above derivative of naphthalene was accomplished in the following manner. The finely-ground ethyl salt was added gradually to three times its weight of concentrated sulphuric acid, the acid being kept well cooled in ice through the addition. When all had been added, the sulphuric acid solution, which had become deep indigo blue in colour, was allowed to stand at the ordinary temperature for about two minutes, when it was poured on to ice. On coming in contact with the ice the blue colour of the solution instantly disappeared, forming a light yellow solution from which, however, no separation of the sulphate of the base took place on standing. The clear solution was therefore made alkaline with ammonia and the yellow oil, which was then precipitated, extracted by means of ether. In order further to purify the base, this ethereal solution was extracted twice with dilute sulphuric acid, and the sulphuric acid extract made alkaline with ammonia. The yellow oil precipitated in this way, and which became solid on standing, was collected by filtration and recrystallised from dilute methyl alcohol, being obtained in small yellow prisms melting at 63° :

0.1282 gave 0.3298 CO_2 and 0.0832 H_2O . $\text{C} = 70.16$; $\text{H} = 7.21$.

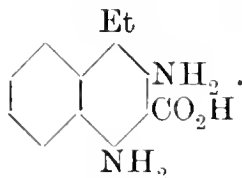
$\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 69.8$; $\text{H} = 7.0$ per cent.

The *hydrochloride*, $C_{15}H_{18}O_2N_2 \cdot 2HCl$, is prepared by dissolving the base in concentrated hydrochloric acid, and allowing the solution to stand. It consists of almost colourless needles :

0.2102 gave 0.1838 AgCl. $Cl = 21.67$.

$C_{15}H_{18}O_2N_2 \cdot 2HCl$ requires $Cl = 21.5$ per cent.

Formation of 2:4-Diamino-1-ethylnaphthalene-3-carboxylic Acid,

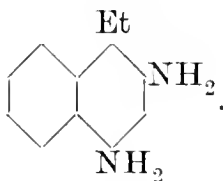


In order to prepare this acid, 4 grams of the ethyl salt were mixed with a methyl alcoholic solution of one-and-a-half times the calculated quantity of potash, and heated on the water-bath until a test portion was completely soluble in water. The product was then diluted with water and evaporated on the water-bath until free from methyl alcohol, when dilute hydrochloric acid was added and the precipitate, which then separated, isolated by filtration. The acid, like those already described, is rapidly decomposed by boiling water. It was therefore crystallised by dissolving it in water at 60° and allowing the solution to cool, when the acid separated in small leaflets which melted and decomposed at about 130° , the observed melting point, however, varied from 128 — 133° with the same specimen, depending on the rapidity with which the temperature was raised :

0.1729 gave 0.4281 CO_2 and 0.0969 H_2O . $C = 67.52$; $H = 6.22$.

$C_{13}H_{14}O_2N_2$ requires $C = 67.8$; $H = 6.1$ per cent.

Formation of 2:4-Diamino-1-ethylnaphthalene.



This base was prepared by heating the carboxylic acid a few degrees above its melting point. The acid was placed in a small flask and heated in a bath of sulphuric acid at 150° until the evolution of carbon dioxide ceased. The residue, which consisted of a viscid red gum, was dissolved in dilute hydrochloric acid and the solution, after being filtered, made alkaline with dilute aqueous caustic soda. The precipitated base, which solidified on standing, was then collected by filtration and recrystallised from dilute methyl alcohol, being obtained in glistening plates melting at 74° :

0.1812 gave 0.5127 CO_2 and 0.1256 H_2O . $\text{C} = 77.17$; $\text{H} = 7.70$.

$\text{C}_{12}\text{H}_{14}\text{N}_2$ requires $\text{C} = 77.4$; $\text{H} = 7.5$ per cent.

The *hydrochloride*, $\text{C}_{12}\text{H}_{11}\text{N}_2 \cdot 2\text{HCl}$, is precipitated as a white, crystalline powder on dissolving the base in concentrated hydrochloric acid and allowing the solution to stand for some time:

0.2207 gave 0.2429 AgCl . $\text{Cl} = 27.31$.

$\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 27.4$ per cent.

The *platinichloride*, $\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$, is formed when a solution of the hydrochloride is mixed with an aqueous solution of platinic chloride. It is a yellow, crystalline powder:

0.2401 gave 0.0781 Pt . $\text{Pt} = 32.53$.

$\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 32.7$ per cent.

Condensation of Benzyl Cyanide with its Sodium Derivative.

As mentioned in the introduction, this condensation was carried out in three different ways, the nitrile being heated with its sodium derivative in alcoholic solution at 100° for (1) half an hour, (2) two hours, (3) twenty-four hours.

(1) *Formation of β -Imino- α -cyano- α -diphenylpropane,* $\text{CH}_2\text{Ph} \cdot \text{C}(\text{NH}) \cdot \text{CH}(\text{CN})\text{Ph}.$

After a number of preliminary experiments it was ascertained that this substance was produced in the greatest yields in the following way. 11.5 grams of sodium were dissolved in 130 grams of alcohol and mixed with 117 grams of benzyl cyanide, the whole being heated on the water-bath for half an hour. After this time the contents of the flask, which had a slight odour resembling ammonia, were mixed with water and the oil which then separated extracted with ether. The ethereal solution after being freed from alcohol by washing with water was, without drying, evaporated free from ether, and then after being mixed with water distilled in a current of steam until all unchanged benzyl cyanide had passed over. The residue, which consisted of a viscid oil, was then extracted by means of ether, and the ethereal solution, after being dried with calcium chloride, evaporated free from ether. The oil which remained was rapidly distilled under reduced pressure and was found to boil at $274^\circ/20$ mm., passing over as a colourless syrup:

0.2016 gave 0.6070 CO_2 and 0.1111 H_2O . $\text{C} = 82.12$; $\text{H} = 6.17$.

$\text{C}_{16}\text{H}_{14}\text{N}_2$ requires $\text{C} = 82.0$; $\text{N} = 6.0$ per cent.

The identity of this compound with that prepared by E. v. Meyer was shown by the fact that with hydroxylamine it gave an oxime melting

at 107°, identical with that formed by the action of this reagent on the ketone, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$. Even when carefully purified by distillation β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane is a viscid liquid and shows no tendency to become crystalline.

(2) *Formation of β -Imino- α -cyano- $\alpha\gamma$ -diphenylpropane,*



β -Keto- α -cyano- $\alpha\gamma$ -diphenylpropane, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CN})\text{Ph}$. Cyanbenzylidine (6-Amino-5-phenyl-2:4-dibenzylpyrimidine) and Ethylamine.

In this experiment the reacting substances were mixed in the same proportions as in experiment (1) but were heated on the water-bath for two hours. The odour resembling ammonia which was apparent at the end of the first half hour, became very marked on further heating, the contents of the flask becoming at the same time dark red. At the end of the specified time a small quantity of alcohol was distilled over and collected in dilute hydrochloric acid, the solution evaporated on the water-bath to a small bulk and mixed with excess of a solution of platinic chloride. On adding a little alcohol to the mixture a yellow precipitate separated out which was collected by filtration and recrystallised from a little hot water, being thus obtained in yellow cubes. The following analysis showed it to be the platinichloride of ethylamine :

0.2713 gave 0.1054 Pt. Pt = 38.85.

$(\text{C}_2\text{H}_5\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6$ requires Pt = 39.0 per cent.

As soon as the small quantity of alcohol necessary for the above experiment had been distilled over, the alcohol solution without further evaporation was mixed with water, acidified with dilute hydrochloric acid and extracted with ether. The ethereal solution after being washed with water to remove alcohol was thoroughly shaken with a solution of three volumes of concentrated hydrochloric acid to one of water.

It was found that by shaking the ethereal solution with this mixture the cyanbenzylidine could be completely extracted in the form of its hydrochloride. This hydrochloride, which is a viscid liquid under ordinary conditions, is quite insoluble in both dilute hydrochloric acid and in ether. Therefore on shaking the ethereal solution with the dilute acid three layers are formed, an upper layer consisting of ethereal solution from which the hydrochloride has been extracted, a middle layer consisting of this hydrochloride in the form of a viscid oil and a lower aqueous layer of dilute hydrochloric acid. The three layers were completely separated in the separating funnel, and it was found that on repeating the process three times the whole of the cyan-

benzylidine present was extracted from the solution. The oily hydrochloride on warming on the water-bath with excess of sodium carbonate solution yielded cyanbenzylidine as a crystalline mass which when recrystallised from absolute alcohol or from light petroleum (b. p. 90—100°) was obtained in slender needles melting at 107°:

0.2076 gave 0.6250 CO₂ and 0.1160 H₂O. C = 82.11; H = 6.25.

C₂₄H₂₁N₃ requires C = 82.0; H = 6.0 per cent.

The properties of cyanbenzylidine have already been described by the investigators mentioned in the introduction. In addition to the published data concerning this substance, we find that it can be distilled under diminished pressure without undergoing any decomposition, passing over at 307° (20 mm.) as a colourless oil which sets to a highly refractive colourless glass on cooling. On dissolving this glass in hot alcohol the solution deposits the original cyanbenzylidine on cooling.*

The *hydrochloride*, C₂₄H₂₁N₃.HCl, was obtained as a crystalline solid in the following way: cyanbenzylidine was dissolved in absolute alcohol containing a small quantity of concentrated hydrochloric acid in which mixture it is readily soluble. Water was then added until a clear solution just remained, when, on standing, the hydrochloride separated in small, colourless needles:

0.1690 gave 0.0640 AgCl. Cl = 9.39.

C₂₄H₂₁N₃.HCl requires Cl = 9.2 per cent.

Cyanbenzylidine is converted into 6-hydroxy-5-phenyl-2:4-dibenzylpyrimidine on heating it with a 10 per cent. sulphuric acid for twenty-four hours. This substance, which was originally prepared by Wache (*J. pr. Chem.*, 1889, [ii], 39, 251), crystallises from alcohol in small needles and melts at 187°:

0.1540 gave 0.4646 CO₂ and 0.0816 H₂O. C = 82.28; H = 5.93.

0.2710 „, 18.8 c.c. nitrogen at 20° and 752 mm. N = 7.88.

C₂₄H₂₀ON₂ requires C = 81.8; H = 5.7; N = 7.9 per cent.

The ethereal solution after the extraction of cyanbenzylidine was, without drying, evaporated free from ether and the residue distilled in a current of steam until free from the small quantity of unchanged

* The stability of cyanbenzylidine is such that it can be distilled at the ordinary pressure without undergoing decomposition boiling under these conditions above 400°. When once melted, it cools to a clear glass, which does not become crystalline except on long standing. We have found this substance extremely useful for determining the melting points of compounds between 230° and 380°, for which purpose it is well adapted since it does not fume and does not become coloured unless kept near its boiling point for some considerable time.

benzyl cyanide, when it was again extracted with ether, the ethereal solution dried by means of calcium chloride and the ether evaporated. The residue, which consisted of a viscid oil, yielded two chief fractions on distillation under diminished pressure. The lower fraction which boiled at 225—230° (20 mm.) solidified on cooling and was purified by recrystallisation from a mixture of benzene and light petroleum (b. p. 70—80°) being obtained in needle clusters, melting at 86° :

0.1566 gave 0.4712 CO₂ and 0.0800 H₂O. C = 82.06 ; H = 5.71.

0.2406 „ 12 c.c. nitrogen at 20° and 756.5 mm. N = 5.70.

C₁₆H₁₃ON requires C = 81.7 ; H = 5.5 ; N = 6.0 per cent.

The analysis and melting point show this substance to be β -keto- α -cyano- $\alpha\gamma$ -diphenylpropane, originally prepared by v. Meyer (*J. pr. Chem.*, 1895, [ii], 52, 115), by the action of sodium ethoxide on a mixture of ethyl phenylacetate and benzyl cyanide, a view which was confirmed by its conversion into the oxime (m. p. 107°) by the action of hydroxylamine.

The higher fraction which boiled constantly at 274° (20 mm.) did not solidify on standing, but from the following analysis evidently consisted of β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane :

0.2013 gave 0.6042 CO₂ and 0.1110 H₂O. C = 81.86 ; H = 6.12.

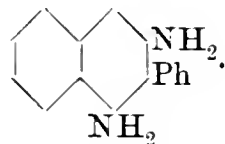
C₁₆H₁₄N₂ requires C = 82.0 ; H = 6.0 per cent.

(3) *Formation of β -Keto- α -cyano- $\alpha\gamma$ -diphenylpropane and Cyanbenzyliline.*

In this experiment the mixture of benzyl cyanide and sodium ethoxide in alcoholic solution was heated for twenty-four hours at 100°, when the odour of ethylamine was hardly apparent. The product was mixed with water and the oil, which then separated, extracted with ether. The ethereal solution, after being washed with water to remove alcohol, was thoroughly washed with a mixture of three parts of concentrated hydrochloric acid to one of water, when the hydrochloride of cyanbenzyliline separated as a middle layer in the manner already described. From this oily hydrochloride the free base was isolated by means of sodium carbonate the yield of cyanbenzyliline obtained in this way being about 60 per cent. of that theoretically possible. The ethereal solution, after being dried by means of calcium chloride, was evaporated free from ether and distilled under diminished pressure. It was found to boil constantly at 225—230° (20 mm.), and on cooling solidified to a crystalline cake which when recrystallised from a mixture of benzene and light petroleum (b. p. 70—80°) yielded β -keto- α -cyano- $\alpha\gamma$ -diphenylpropane, melting at 86°. There is, therefore, apparently no β -imino- α -cyano- $\alpha\gamma$ -diphenylpropane formed under these experimental conditions,

the amount produced in the first instance having either condensed with unchanged benzyl cyanide to form cyanbenzylidine, or having passed into β -keto- α -cyano- γ -diphenylpropane through the "hydrolysis" of the imino-group.

Formation of 1:3-Diamino-2-phenylnaphthalene,



The transformation of β -imino- α -cyano- γ -diphenylpropane into 1:3-diamino-2-phenylnaphthalene was effected in the following manner: five grams of the liquid nitrile were added gradually to 15 grams of concentrated sulphuric acid, the solution being kept well cooled throughout the addition, since the liquid, which dissolved rapidly in the concentrated acid, caused a considerable rise in temperature. When all had dissolved, the solution, which was dark brown, was allowed to stand at the ordinary temperature for from three to four minutes and then poured into a large volume of water. The solution thus obtained, after being filtered to remove any impurities, was made alkaline with ammonia, and the base, which was then precipitated, collected by filtration and purified by recrystallisation from methyl alcohol or benzene. 1:3-Diamino-2-phenylnaphthalene crystallises in colourless, glistening plates melting at 116° :

0.1564 gave 0.4699 CO_2 and 0.0853 H_2O . $\text{C} = 81.94$; $\text{H} = 6.10$.

0.3238 ,, 32.6 c.c. nitrogen at 15.8° and 758.4 mm. $\text{N} = 11.73$.

$\text{C}_{16}\text{H}_{14}\text{N}_2$ requires $\text{C} = 82.0$; $\text{H} = 6.0$; $\text{N} = 12.0$ per cent.

The base becomes slowly coloured red on exposure to the air. It is easily soluble in alcohol or benzene, sparingly so in cold ether, and insoluble in light petroleum. Its solutions exhibit a marked blue fluorescence.

The *hydrochloride* is precipitated in fine feather-like needles on dissolving the base in a little dilute hydrochloric acid, and, after adding an equal volume of concentrated hydrochloric acid, allowing the solution to stand:

0.2211 gave 0.2043 AgCl . $\text{Cl} = 22.92$.

$\text{C}_{16}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ requires $\text{Cl} = 23.1$ per cent.

The hydrochloride is rapidly coloured red on exposure to light.

The *diacetyl* derivative, $\text{C}_{16}\text{H}_{12}\text{N}_2(\text{Ac})_2$, is best prepared by boiling the base with excess of acetyl chloride until all has passed into solution. A considerable quantity of acetyl chloride is necessary for this purpose, since the acetyl derivative is only sparingly soluble in this reagent. When all had dissolved the solution was cooled and allowed

to stand, the crystalline precipitate which then separated being isolated by filtration and purified by dissolving in alcohol and diluting the solution with water. On standing, the *acetyl* derivative separated in small needles, melting at 267° :

0.1743 gave 0.4805 CO_2 and 0.0928 H_2O . $\text{C} = 75.18$; $\text{H} = 5.96$.

$\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 75.5$; $\text{H} = 5.7$ per cent.

The *acetyl acetate*, $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Ac}, \text{CH}_3 \cdot \text{CO}_2\text{H}$, was formed in an attempt to prepare the diacetyl derivative by the action of acetic anhydride on the base.

1:3-Diamino-2-phenylnaphthalene was boiled with excess of acetic anhydride for two hours and the solution evaporated in an evacuated desiccator over caustic potash. The gummy residue became completely solid on scratching, and when recrystallised from absolute alcohol was obtained in small prisms melting at 185° :

I. 0.1847 gave 0.4864 CO_2 and 0.0969 H_2O . $\text{C} = 71.82$; $\text{H} = 5.87$

II. 0.1872 „ 0.4931 CO_2 „ 0.0988 H_2O . $\text{C} = 71.84$; $\text{H} = 5.90$.

$\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2$ requires $\text{C} = 71.4$; $\text{H} = 5.9$ per cent.

Other derivatives of this base are still under investigation.

Much of the expense entailed by this research has been met by a grant from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

MANCHESTER UNIVERSITY.

CLXXXVI.—A *New Trinitroacetaminophenol and its use as a Synthetical Agent.*

By RAPHAEL MELDOLA, F.R.S.

IN the course of some experiments having for their object the preparation of Reverdin's dinitroaminophenol of m. p. $230-231^{\circ}$, referred to in a former paper by one of the authors and F. G. C. Stephens (Trans., 1905, 87, 1206), it was found that the nitration of diacetyl-*p*-aminophenol (*p*-acetaminophenyl acetate) gave rise under most conditions to the mononitro-derivative, $\text{OAc}:\text{NO}_2:\text{NHAc} = 1:3:4$, corresponding to the *m*-nitro-*p*-aminophenol of Hähle (*J. pr. Chem.*, 1891, [ii], 43, 63 ; see also the recent paper by Reverdin and Bucky, *Ber.*, 1906, 39, 2687). In attempting to nitrate this mono-

nitrodiacetyl-*p*-aminophenol so as to obtain the required dinitro-compound, it was found that under certain conditions a trinitro-derivative was produced, and as this compound was found to possess remarkably active properties as a synthetical agent, it has been and is being made the subject of a special investigation. Some of the results so far obtained are made known in the present paper.

In order to prepare the new trinitro-compound, fuming nitric acid is mixed with an equal volume of strong sulphuric acid and the mixture cooled by immersion of the beaker in melting ice. The mononitrodiacetyl compound is introduced into the mixed acids in small portions until the solution is nearly saturated, and the trinitro-compound is then precipitated by pouring the acid solution on to ice. The product, after being collected and washed, is best purified by crystallisation from glacial acetic acid. It crystallises in yellow needles melting with decomposition at 178—179°.* The compound is soluble in boiling alcohol or acetone, and dissolves slightly in boiling water, from which it separates on cooling in slender, yellow needles:

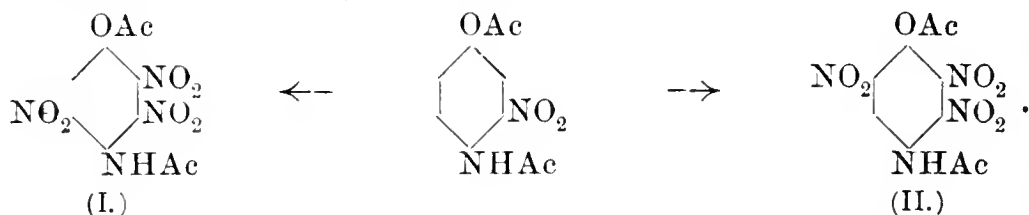
0.0887 gave 14.9 c.c. moist nitrogen at 15° and 753.8 mm. N = 19.51.

0.1037 „ 16.9 c.c. „ 12° „ 759.8 mm. N = 19.34.

$C_8H_6O_8N_4$ requires N = 19.63 per cent.

It is not absolutely necessary in preparing this compound to divide the process of nitration into two stages. The trinitro-derivative can also be prepared directly by dissolving diacetyl-*p*-aminophenol in the mixture of acids as above. Under these conditions, however, a considerable excess of the acid mixture must be used in order to obtain a good yield. The constitution of the trinitro-compound is determined by the following considerations.

A mononitro-derivative of the constitution stated can only give rise theoretically to two possible trinitro-derivatives:

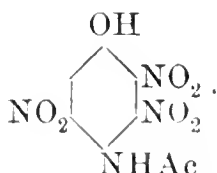


The first of these formulæ represents the compound as arising from the introduction of a third nitro-group into Reverdin's 3:5-dinitro-compound and the second (II) as arising by a similar process from 2:6-dinitro-*p*-acetaminophenol, that is, as a derivative of *isopicramic* acid. Experiments have shown that the acetyl derivative of *isopicramic* acid cannot be further nitrated, whereas the 3:5-dinitrodiacetyl com-

* All melting points given in this paper were corrected by reference to standard short-stemmed thermometers having the certificate of the Reichsanstalt, Berlin.

pound is quite readily converted by a mixture of nitric and sulphuric acids into the new trinitro-compound.

The orienting influence of the acetoxy-group is paramount in determining the entry of the first nitro-group into position 3, and the joint influence of the nitro- and acetoxy-groups determines the entry of the second nitro-group into position 5, giving Reverdin's compound, from which the new trinitro-compound arises. That the acetoxy-group is all important is shown by the now well-known fact that *p*-acetaminophenol itself always gives rise to *isopieramic acid* on nitration, and the most recent observation by Reverdin and Bucky confirms this in a very striking manner. In the description of the practical details of nitration given above, it will be noted that the diacetyl-*p*-aminophenol or its 3-nitro-derivative is introduced directly into the cooled mixture of acids. In Reverdin and Bucky's process, the diacetyl compound is first dissolved in strong sulphuric acid, and the solution thus obtained is then treated with the nitric acid mixture. In these circumstances, as the authors point out, the diacetyl compound undergoes hydrolysis by the sulphuric acid at the first stage, so that the nitric acid is really acting on *p*-acetaminophenol, and the resulting compound is accordingly *isopieramic acid* (*Ber.*, 1906, 39, 2687). The entry of the third nitro-group in the process now made known appears also to loosen the attachment of the acetyl group as hydrolysis simultaneously takes place and the new compound is accordingly :

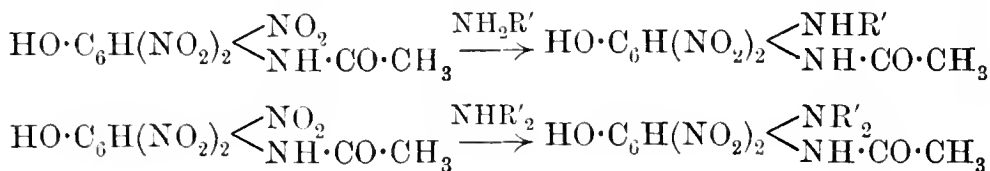


2 : 3 : 5-Trinitro-4-acetaminophenol.

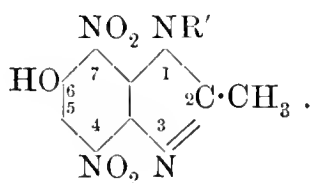
Properties of the Trinitro-compound.—As might be inferred from its formula, the new compound is strongly phenolic in character. It forms highly-coloured salts of an orange-red colour, but owing to the readiness with which the substance is decomposed by bases, none of these salts could be isolated, nor has it been possible to alkylate or acylate the hydroxyl group. Attempts to remove the acetyl group so as to obtain the trinitroaminophenol also gave only resinous products of decomposition. When sulphuric acid was used as a hydrolysing agent, a small quantity of a crystalline compound was obtained, which on examination proved to be a highly explosive diazo-oxide, resulting no doubt from the simultaneous hydrolysis and diazotisation of the product by one of the nitro-groups removed by the hydrolysing agent, so that in this case also decomposition takes place.

Synthesis of Anhydro-bases.

Previous experience with compounds containing a displaceable nitro-group led to the conclusion that in the new trinitroacetaminophenol one of the nitro-groups 2 or 3 would be easily eliminated. It might, for instance, be predicted with certainty that if the corresponding trinitro-*p*-anisidine could be obtained this compound on diazotisation would lose the 3-nitro-group. The instability of the salts and the ready decomposability of the trinitro-compound in the presence of basic substances distinctly pointed to the conclusion that these properties were due to the mobile character of one of the nitro-groups, since polynitro-derivatives of phenols as a rule form stable salts with bases. It therefore seemed probable that under regulated conditions the mobile nitro-group might be replaceable by amine residues giving rise to compounds of the following types :



If, moreover, as seemed most probable, it was the 3-nitro-group which was the mobile group, decompositions taking place according to the first of the above schemes might be expected to give rise to anhydro-bases by the interaction of the ortho-groups. Such compounds would be derivatives of substituted benziminazole and might be thus formulated * :



Experiments with various amines showed that the new trinitro-compound most readily interacted with primary amines both fatty and aromatic, but that no action took place under similar conditions with secondary or tertiary bases. The products consisted of anhydro-bases mixed in some instances with the non-anhydridised compound, thus proving that it is the 3-nitro-group which is replaced. Of the amines thus far tried, positive results have been obtained with ammonia, ethylamine, aniline, α - and β -naphthylamine, benzylamine, and piperidine. Negative results were given by dimethylaniline, diphenylamine, and pyridine. As these iminazoles promise to be of

* I have adopted the numbering of the atoms in the ring system given in Richter's "Lexikon."

special interest from several points of view, it is proposed to continue their investigation in detail, and the present results are made known as a preliminary contribution to the subject. The compound formed by the action of ammonia, although theoretically the simplest member of the group of substituted iminazoles herein dealt with, will require further investigation before its constitution can be established. In all the reactions the nitro-group is probably eliminated in the form of nitrous acid which reacts with the excess of amine with the production of an azo-compound, an alcohol, or simply a salt, according to the nature of the amine. As the compounds described in this paper are all formed by the substitution of various radicles for R' in the NR' group in the iminazole ring in the foregoing formula, the constitution will be sufficiently expressed by the systematic name without repeating the formula for each compound.

4:7-Dinitro-6-hydroxy-1-phenyl-2-methylbenziminazole.—The trinitro-compound reacts readily with aniline under all conditions. In concentrated alcoholic solution the action is so energetic that spontaneous ebullition takes place. In order to prepare the above phenyl derivative in quantity the trinitro-compound is dissolved in a considerable excess of alcohol and to the hot solution an excess of aniline is gradually added. A deep orange colour is at once developed, and on cooling the solution deposits the iminazole in ochreous needles. After being collected and washed with alcohol and purified by crystallisation from glacial acetic acid, the pure substance crystallises in transparent, yellow prisms, which become opaque on being washed with alcohol. From alcohol it crystallises in flat, yellow needles.

The compound is soluble in all the ordinary organic solvents and is phenolic in character, dissolving in aqueous alkali with an orange colour and being precipitated unchanged by acids. It possesses a feebly basic character, its salts being readily dissociated by water. The melting point is 188—189°:

0.1053 gave 16 c.c. moist nitrogen at 15° and 753.2 mm. N = 17.63.

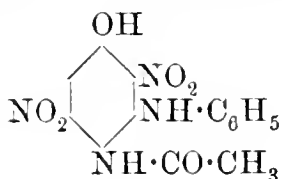
0.1007 „ 15.3 c.c. „ „ „ 16° „ 765.9 mm. N = 17.85.

$C_{14}H_{10}O_5N_4$ requires N = 17.87 per cent.

The same compound is also obtained when glacial acetic acid is used as a solvent or when the trinitro-derivative is dissolved in excess of aniline and allowed to stand for some days at the ordinary temperature. In both these cases aminoazobenzene was found among the products and was easily separated from the iminazole by taking advantage of the phenolic character of the latter. When aniline acts on the trinitro-compound in alcoholic solution, as in the method of preparation found most advantageous, there is also formed with the iminazole, which is the main product, a small quantity of another substance which is partly

contained in the mother liquor, from which on standing it separates in the form of deep orange prisms. Some of the same compound is easily seen in admixture with the crude iminazole but is removed in the course of purification by crystallisation from acetic acid. This secondary product is no doubt the non-anhydridised compound, namely,

3 : 6-Dinitro-2-acetamino-5-hydroxydiphenylamine :



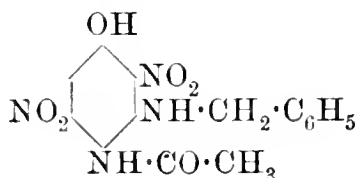
This substance is also phenolic and dissolves in alkali with an orange colour. It crystallises from acetic acid in red, prismatic needles melting at 179° :

0.0968 gave 14 c.c. moist nitrogen at 12° and 744.9 mm. $\text{N} = 16.82$.

$\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_4$ requires $\text{N} = 16.86$ per cent.

Only a small quantity of this compound has as yet been isolated and it is proposed to obtain a larger supply for further investigation.

4 : 7-Dinitro-6-hydroxy-1-benzyl-2-methylbenziminazole.—A concentrated alcoholic solution of the trinitro-compound is mixed with an alcoholic solution of benzylamine containing the latter base in excess, when a reaction at once takes place with the development of sufficient heat to cause ebullition. The solution when cold solidifies to a crystalline pulp of orange needles. In order to purify the crude product the crystals were collected, washed with dilute hydrochloric acid and crystallised from alcohol. The orange colour of the deposited crystals immediately disappears on washing with acid, thus indicating that the compound is a benzylamine salt. After treatment with acid and crystallisation from alcohol, the pure compound presents the appearance of flat, silky needles of a greenish-yellow colour. The melting point is 207° . Analysis indicated that in this case the first product is the dinitroacetaminohydroxyphenylbenzylamine :



0.0886 gave 12.2 c.c. moist nitrogen at 14° and 763.3 mm. $\text{N} = 16.29$.

$\text{C}_{15}\text{H}_{14}\text{O}_6\text{N}_4$ requires $\text{N} = 16.22$ per cent.

This substance is sufficiently basic to dissolve in strong mineral acids, but the salts formed with such acids are dissociated by an excess of water. The compound is also phenolic, dissolving in alkalis with an

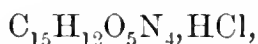
orange colour. An attempt to eliminate the acetyl group by boiling the solution of the sodium salt showed that some more complex decomposition takes place with the formation of benzaldehyde. A beautiful, crystalline, ammonium salt consisting of bright orange, prismatic needles is formed by the action of ammonia. When this salt is crystallised from boiling water and then decomposed by treatment with an acid the recovered substance is not the original phenylbenzylamine derivative but the iminazole, so that anhydridisation takes place on boiling the ammonium salt with water. The iminazole is also formed by dissolving the phenylbenzylamine compound in strong sulphuric acid, heating the solution for a few minutes to 100° and then pouring into water. The compound thus obtained crystallises from alcohol in yellow needles melting at 156° :

0.1048 gave 15.2 c.c. moist nitrogen at 15° and 770.6 mm. $N = 17.22$.

0.1195 „ 17.3 c.c. „ „ 14° „ 762 mm. $N = 17.07$.

$C_{15}H_{12}O_5N_4$ requires $N = 17.11$ per cent.

This iminazole is both phenolic and basic. The alkali salts are orange in colour; the ammonium salt is much more soluble than the ammonium salt of the original phenylbenzylamine derivative. The substance dissolves in hydrochloric acid and the solution on the addition of strong acid deposits white needles of the hydrochloride,



which are stable only in the presence of excess of acid.

4:7-Dinitro-6-hydroxy-2-methyl-1-ethylbenziminazole.—On adding an alcoholic solution of ethylamine to the trinitro-compound suspended in alcohol an orange solution is at once obtained, and this soon solidifies to a crystalline pulp of the ethylamine salt of the trinitroacetaminophenol. In order to bring about the iminazole formation, the solution must be heated on the water-bath for some hours. The product is best isolated by collecting the crystalline deposit which separates on cooling, and which consists of the ethylamine salts of the iminazole with some of the ethylamine salt of the phenylethylamine derivative, washing with alcohol, then with dilute hydrochloric acid and finally with water. At this stage the product consists of a mixture of the iminazole with the non-anhydridised compound and, if the former is required, it is better to ensure complete anhydridisation by dissolving the dry product in a little strong sulphuric acid, heating for a few minutes on the water-bath and then pouring into water. After crystallisation from alcohol the compound consists of orange, nodular crystals melting with decomposition at 215° :

0.1335 gave 23 c.c. moist nitrogen at 13° and 776 mm. $N = 20.79$.

$C_{10}H_{10}O_5N_4$ requires $N = 21.09$ per cent.

This iminazole forms orange salts with alkalis, the ammonium salt

crystallising readily from hot water in bright orange-red needles. The compound is also basic, dissolving in mineral acids with the formation of colourless salts which are stable only in presence of excess of acid.

4 : 7-Dinitro-6-hydroxy-1- α -naphthyl-2-methylbenziminazole.—The trinitro-compound and α -naphthylamine in excess are heated together in alcoholic solution for some hours on the water-bath, the reaction in this case being less energetic and the yield of iminazole smaller than in the case of the other amines. The whole solution after completion of the reaction is poured into very dilute hydrochloric acid, filtered to remove excess of naphthylamine, the precipitate washed with water, and then extracted with dilute sodium hydroxide and again filtered. The latter treatment separates the iminazole from the α -aminoazonaphthalene with which it is mixed, the orange alkaline filtrate giving the required compound on acidifying. After crystallisation from alcohol the iminazole was obtained in ochreous, hexagonal tablets melting with decomposition at 241° :

0.0873 gave 11.2 c.c. moist nitrogen at 10° and 766.9 mm. $N = 15.50$.

$C_{18}H_{12}O_5N_4$ requires $N = 15.42$ per cent.

No formation of the intermediate α -naphthylphenylamine derivative was observed in this case.

4 : 7-Dinitro-6-hydroxy-1- β -naphthyl-2-methylbenziminazole.—The reaction in this case is also sluggish and the mode of procedure, both with respect to the formation of the iminazole and its isolation, was similar to that adopted for the α -naphthylamine compound. In this case β -aminoazonaphthalene is also formed together with a certain quantity of the β -naphthylphenylamine derivative. The latter can be removed by crystallisation of the mixed product from glacial acetic acid after having previously separated the aminoazo-compound by alkaline extraction. From acetic acid the iminazole separates slowly in two forms, brown nodules and ochreous prisms, both forms melting with decomposition at 242° :

0.1088 gave 13.9 c.c. moist nitrogen at 11° and 763 mm. $N = 15.29$.

$C_{18}H_{12}O_5N_4$ requires $N = 15.43$ per cent.

4 : 7-Dinitro-6-hydroxy-1-*m*-nitrophenyl-2-methylbenziminazole.—In order to prepare this compound the trinitroacetaminophenol is boiled in alcoholic solution with an excess of *m*-nitroaniline for a few minutes and the solution then kept gently heated on the water-bath for some hours. The product separates out in yellow needles, which are collected, washed with alcohol, and purified by extraction with aqueous alkali and, after filtration of the solution, precipitation by acid. The substance is only sparingly soluble in boiling alcohol and is best purified by repeated crystallisation from glacial acetic acid from which

it separates in two forms, light, ochreous, nodular aggregates of short, slender needles and brown, nodular aggregates of stumpy needles. Both forms have the same melting point, 242—243° with decomposition :

0.1181 gave 19.3 c.c. moist nitrogen at 13° and 752.6 mm. $N = 19.40$.

$C_{14}H_9O_7N_5$ requires $N = 19.54$ per cent.

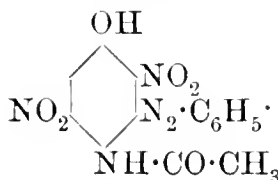
The compound is slightly basic and distinctly phenolic in character, the alkali salts dissolving in water with a yellow colour. The silver salt was obtained as an ochreous powder by adding a solution of silver nitrate to a solution of the ammonium salt :

0.1369, on ignition, gave 0.0319. $Ag = 23.3$.

$C_{14}H_8O_7N_5Ag$ requires $Ag = 23.15$ per cent.

Synthesis of Azo-compounds.

The trinitro-compound reacts readily with hydrazines, with the formation of hydrazo-compounds which pass by oxidation into azo-compounds. As a typical case the action of phenylhydrazine has been studied and the resulting compound isolated. Its composition and properties indicate that it is a derivative of hydroxyazobenzene :



In order to prepare this substance the trinitro-compound is heated with an alcoholic solution containing an excess of phenylhydrazine as long as nitrogen is evolved. On cooling, a crystalline pulp of red needles is obtained. After being collected and washed with alcohol, the substance can be purified by crystallisation from alcohol, from which solvent it separates in red needles decomposing at about 188° :

0.1091 gave 19.4 c.c. moist nitrogen at 14° and 750 mm. $N = 20.33$.

$C_{14}H_{11}O_6N_5$ requires $N = 20.63$ per cent.

This azo-compound is of interest on account of its instability ; it is decomposed on boiling with glacial acetic acid and also by alkalis. The compound itself and the products of its decomposition are undergoing investigation.

During the first part of this research I had the assistance of Mr. F. G. C. Stephens, and during the latter part that of Mr. J. G. Hay, to both of whom I desire to express my thanks.

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ERRATA.

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1567	12	„ "orthosilicate" read "metasilicate."
1568	<i>et seq.</i>	„ "Scherer" read "Scheerer."
1569	12	„ "Chantelope" read "Chantelope."
„	16	„ "Zi" read "Zr."
1935	7*	„ "one of the authors" read "the author."

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